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DIRECT/DELAYED RESPONSE PROJECT: QUALITY ASSURANCE REPORT FOR PHYSICAL AND CHEMICAL ANALYSES OF SOILS FROM THE NORTHEASTERN UNITED STATES

by

G.E. Byers, R.D. Van Remortel, J.E. Teberg, M.J. Miah, C.J. Palmer,
M.L. Papp, W.H. Cole, A.D. Tansey, D.L. Cassell, and P.W. Shaffer

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The Northeastern Soil Survey was conducted during 1985 as a synoptic physical and chemical survey to characterize a statistical sampling of watersheds in a region of the United States believed to be susceptible to the effects of acidic deposition. This document addresses the implementation of a quality assurance program and the verification of the analytical data base for the Northeastern Soil Survey. It is focused primarily towards the users of the data base who will be analyzing the data and making various assessments and conclusions relating to the effects of acidic deposition on the soils of the Northeastern region of the United States. The quality assurance program is evaluated in terms of its success in identifying potential problems that could have an effect on the quality of the data. Verification procedures used to analyze laboratory data are described. Quality is assessed by describing the detectability, precision, accuracy (interlaboratory differences), representativeness, completeness, and comparability of the data for the quality assurance samples used throughout the soil survey. Detection limits and two-tiered precision data quality objectives were established for most of the parameters. A step-function statistical approach was used to assess precision.

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This document is one volume of a set which fully describes the Direct/Delayed Response Project, Northeastern Soil Survey. The complete document set includes the major data report, quality assurance plan, laboratory analysis handbook, field and laboratory operations reports, and quality assurance reports. Similar sets are being produced for each Aquatic Effects Research Program component project. Colored covers, artwork, and the use of the project name in the document title serve to identify each companion document set.

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[1] Lockheed Engineering & Sciences Company, Las Vegas, Nevada 89119.

[2] Environmental Research Center, University of Nevada, Las Vegas, Nevada 89114.

[3] NSI Technology Services Corporation, Corvallis, OR 97333.

Abstract

The Direct/Delayed Response Project is designed to address the concern over potential acidification of surface waters by atmospheric sulfur deposition within the United States. The Northeastern Soil Survey was conducted during 1985 as a synoptic physical and chemical survey to characterize a statistical sampling of watersheds in a region of the United States believed to be susceptible to the effects of acidic deposition. This document addresses the implementation of a quality assurance program and the verification of the analytical data base for the Northeastern Soil Survey. It is focused primarily towards the users of the data base who will be analyzing the data and making various assessments and conclusions relating to the effects of acidic deposition on the soils of the northeastern region of the United States.

The quality assurance program is evaluated in terms of its success in identifying potential problems that could have an effect on the quality of the data. Verification procedures used to analyze laboratory data are described. Quality is assessed by describing the detectability, precision, accuracy (interlaboratory differences), representativeness, completeness, and comparability of the data for the quality assurance samples used throughout the soil survey. Three types of quality assurance samples and six types of quality control samples were used in the Northeastern Soil Survey.

The fifty-one parameters in the data base are segregated into nine groups to allow comparison among similar parameters. Detection limits and two-tiered precision data quality objectives were established for most of the parameters. A step-function statistical approach was used to assess precision. Conclusions and recommendations are provided at the end of the report. The recommendations will be useful in the planning of future projects of this nature.

This report is submitted in partial fulfillment of Contract Number 68-03-3249 by Lockheed Engineering & Sciences Company, Las Vegas, Nevada, under sponsorship of the U. S. Environmental Protection Agency.

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List of Acronyms and Abbreviations

AA	atomic absorption
ADS	Acid Deposition System
AERP	Aquatic Effects Research Program
AC_BACL	exchangeable acidity in barium chloride triethanolamine
AC_KCL	exchangeable acidity in potassium chloride
AL_AO	extractable aluminum in acid oxalate
AL_CD	extractable aluminum in citrate dithionite
AL_CL2	extractable aluminum in calcium chloride
AL_KCL	exchangeable aluminum in potassium chloride
AL_PYP	extractable aluminum in sodium pyrophosphate
ANOVA	analysis of variance
AS	audit samples
CA_CL	exchangeable calcium in ammonium chloride
CA_CL2	extractable calcium in calcium chloride
CA_OAC	exchangeable calcium in ammonium acetate
CEC	cation exchange capacity
CEC_CL	cation exchange capacity by ammonium chloride
CEC_OAC	cation exchange capacity by ammonium acetate
CLAY	total clay fraction
CLP	Contract Laboratory Program
CRDL	Contract-required detection limit
COS	coarse sand fraction
COSI	coarse silt fraction
C_TOT	total carbon
DDRP	Direct/Delayed Response Project
DFFITS	Difference of fit statistic
DL	detection limit
DL-QCCS	detection limit quality control check sample
DQO	data quality objective
EGME	ethylene glycol monoethyl ether
EMSL-LV	Environmental Monitoring Systems Laboratory at Las Vegas, Nevada
EPA	U.S. Environmental Protection Agency
ERL-C	Environmental Research Laboratory at Corvallis, Oregon
FD	field duplicate sample
FE_AO	extractable iron in acid oxalate
FE_CD	extractable iron in citrate dithionite
FE_CL2	extractable iron in calcium chloride
FE_PYP	extractable iron in pyrophosphate
FIA	flow injection analysis
FP	flame photometry
FSI	fine silt fraction
FS	fine sand fraction
GIS	geographic information system
IC	ion chromatography
ICP	inductively coupled argon plasma

List of Acronyms and Abbreviations (Continued)

IDL	instrument detection limit
IFB	invitation for bid
K_CL	exchangeable potassium in ammonium chloride
K_CL2	extractable potassium in calcium chloride
K_OAC	exchangeable potassium in ammonium acetate
MG_CL	exchangeable magnesium in ammonium chloride
MG_CL2	extractable magnesium in calcium chloride
MG_OAC	exchangeable magnesium in ammonium acetate
MOIST	percent air-dry soil moisture content
MS	medium sand fraction
MQO	measurement quality objectives
NA_CL	exchangeable sodium in ammonium chloride
NA_CL2	extractable sodium in calcium chloride
NA_OAC	exchangeable sodium in ammonium acetate
NAPAP	National Acid Precipitation Assessment Program
NCC	National Computer Center
NE	Northeast
NSWS	National Surface Water Survey
N_TOT	total nitrogen
ORNL	Oak Ridge National Laboratory
PD	preparation duplicate sample
PE	performance evaluation
PH_H2O	pH in deionized water
PH_002M	pH in 0.002M calcium chloride
PH_01M	pH in 0.01M calcium chloride
QA	quality assurance
QA/QC	quality assurance/quality control
QC	quality control
QCCS	quality control check sample
RS	routine sample
RSD	relative standard deviation
SAND	total sand fraction
SAS	Statistical Analysis Systems, Inc.
SBRP	Southern Blue Ridge Province
SCS	Soil Conservation Service
SD	standard deviation
SDL	system detection limit
S/H	sampling class/horizon
SILT	total silt fraction
SO4_0	zero mg S/L sulfate isotherm parameter
SO4_2	two mg S/L sulfate isotherm parameter
SO4_4	four mg S/L sulfate isotherm parameter
SO4_8	eight mg S/L sulfate isotherm parameter
SO4_16	sixteen mg S/L sulfate isotherm parameter
SO4_32	thirty-two mg S/L sulfate isotherm parameter
SO4_H2O	extractable sulfate in water
SO4_PO4	extractable sulfate in sodium phosphate
SOW	statement of work
SP_SUR	specific surface area
SR	Studentized Residual
S_TOT	total sulfur
USDA	U.S. Department of Agriculture
VCOS	very coarse sand fraction
VFS	very fine sand fraction

Project Summary

Introduction

The U.S. Environmental Protection Agency (EPA), as a participant in the National Acid Precipitation Assessment Program, has designed and implemented a research program to predict the long-term response of watersheds and surface waters in the United States to acidic deposition. Based on this research, a sample of watershed systems will be classified according to the time scale in which each system will reach an acidic steady state, assuming current levels of acidic deposition. The Direct/Delayed Response Project (DDRP) was designed as the terrestrial component of the EPA Aquatic Effects Research Program.

The mapping for the DDRP Northeastern Soil Survey was conducted during the Spring and Summer of 1985 and the sampling took place the during Summer and Fall of 1985. These activities initiated the first full-scale regional survey of the DDRP. The physical and chemical properties that were measured in the soil samples are listed below.

PHYSICAL AND CHEMICAL PROPERTIES MEASURED IN THE DIRECT/DELAYED RESPONSE PROJECT NORTHEASTERN SOIL SURVEY

Air-dry Moisture Content
Specific Surface Area
Total Sand
Very Coarse Sand
Coarse Sand
Medium Sand
Fine Sand
Very Fine Sand
Total Silt
Coarse Silt
Fine Silt
Total Clay
pH in Deionized Water
pH in 0.002M $CaCl_2$
pH in 0.01M $CaCl_2$

Ca in 1.0M Ammonium Chloride
Mg in 1.0M Ammonium Chloride
K in 1.0M Ammonium Chloride
Na in 1.0M Ammonium Chloride
Ca in 1.0M Ammonium Acetate
Mg in 1.0M Ammonium Acetate
K in 1.0M Ammonium Acetate
Na in 1.0M Ammonium Acetate
CEC in 1.0M Ammonium Chloride
CEC in 1.0M Ammonium Acetate
Ex. Acidity by 1.0M KCl
Ex. Acidity by $BaCl_2$-TEA
Ext. Aluminum in 1.0M KCl
Ca in 0.002M Calcium Chloride
Mg in 0.002M Calcium Chloride
K in 0.002M Calcium Chloride
Na in 0.002M Calcium Chloride
Fe in 0.002M Calcium Chloride

Al in 0.002M Calcium Chloride
Ext. Fe in Pyrophosphate
Ext. Al in Pyrophosphate
Ext. Fe in Ammonium Oxalate
Ext. Al in Ammonium Oxalate
Ext. Fe in Citrate Dithionite
Ext. Al in Citrate Dithionite
Ext. Sulfate in Deionized Water
Ext. Sulfate in Sodium Phosphate
Sulfate Isotherm 0 mg sulfur/L
Sulfate Isotherm 2 mg sulfur/L
Sulfate Isotherm 4 mg sulfur/L
Sulfate Isotherm 8 mg sulfur/L
Sulfate Isotherm 16 mg sulfur/L
Sulfate Isotherm 32 mg sulfur/L
Total Carbon
Total Nitrogen
Total Sulfur

Data Quality Objectives and Assessment

The quality assurance (QA) program, soil sampling techniques, sample preparation, and analytical methods, were designed to satisfy the data quality objectives (DQOs) for field and analytical data and to assess the variability of sampling, preparation, and analytical performance. The DQOs for this survey were directed toward detectability, precision, and completeness. Accuracy, representativeness, and comparability of the data were also assessed, although specific DQOs were not imposed on these attributes.

Detectability

The instrument detection limit is the lowest value that an analytical instrument can reliably detect above instrument background concentrations and was calculated for each analyte as three times the standard deviation of a low level quality control check sample, under the assumption that its variability would approximate the variability of an analytical blank sample. The system detection limit indicates the variability of a blank sample resulting from sample collection, processing, extraction, and analysis. The system detection limit was estimated for each parameter as the variability in the ten percent of field duplicates that had the lowest concentration of the analyte of interest. Contracts with the analytical laboratories established maximum allowable instrument detection limits, defined as contract-required detection limits; however, no DQOs were established for system detectability.

Precision

Precision is the degree of scatter of repeated measurements. Measurement imprecision is distinct from the overall variability in the population itself. Determination of measurement imprecision and its sources in the Northeastern Soil Survey relied strongly on the analyses of the

QA samples and was a function of the intralaboratory within-batch precision DQOs defined in the QA Plan. Overall variability (measurement and population) was estimated from the routine data. No DQOs were established for the sampling or preparation phases of the survey.

The precision DQOs were characterized by use of a two-tiered system. Below a specific concentration, called the knot, precision is defined as a standard deviation in absolute reporting units; above the knot, precision is defined as a percent relative standard deviation. In order to address the issue of concentration-dependent variance, the range of soil analyte concentrations was divided into appropriate intervals (windows) within which the error variance was relatively constant. A step function was fitted across the windows to represent the error variance for the entire concentration range. Different step functions were used to assess the variability for each QA sample type. The data uncertainty in the routine samples due to collection error was also measured.

Accuracy (Interlaboratory Differences)

Accuracy is the ability of a measurement system to approximate a true value. Accuracy could not be determined because the audit samples used in the survey were natural soil samples with chemical composition and physical properties that were not known with any confidence. Due to this lack of acceptable values for accuracy estimates, the data were assessed only for interlaboratory differences.

Three types of comparisons made were: (1) the use of a pair-wise statistical test for significance between laboratories; (2) the pooling of audit sample data for each laboratory for direct interlaboratory comparisons; and (3) the pooling of laboratory data for each audit sample for comparison of laboratory performance among audit samples.

Representativeness

The representativeness objectives of the survey were qualitative in nature. The general objectives were that: (1) the soil samples collected by the field crews be representative of the soil sampling class characteristics, (2) the samples be homogenized and subsampled properly by the preparation laboratory, and (3) the QA duplicate samples adequately represent the range of analyte concentrations found in the routine samples.

Completeness

The 100 percent completeness objectives of the survey were to determine whether (1) all pedons designated for sampling were actually sampled by the field crews, (2) all samples received by the preparation laboratories were prepared and analyzed, and (3) all samples received by the analytical laboratories were analyzed and that 90 percent of the required measurements were made on all samples. Enough data were provided to allow statistically significant conclusions to be drawn. Data qualifiers, or flags, for completeness were inserted in the data base to indicate any missing values.

Comparability

Data comparability objectives were qualitative in nature. The goal was for comparability of data from the soil surveys within the DDRP and for the DDRP surveys to be comparable to other similar programs. The stated objective was the uniform use of known, accepted, and documented procedures for site location, soil sample collection, sample preparation, extraction, analysis, and standard reporting units for the Northeastern Soil Survey. Uniform QA/QC protocols and on-site inspections assured that these procedures were implemented properly. The resulting analytical data should be comparable to those from other surveys.

Quality Assurance and Quality Control Samples

Quality assurance samples were used to independently assess data quality and monitor the internal quality control (QC) procedures. The composition and identity of the QA samples were unknown to the analyst. Three types of QA samples were used in the Northeastern Soil Survey: (1) field duplicates (soil samples were collected by each sampling crew from one horizon of one pedon each day and were placed randomly in the sample batch with the other samples from the same pedon); (2) preparation duplicates (one soil sample per sample batch was selected and split by the preparation laboratory and placed randomly in the sample batch); and (3) natural audit samples, (one duplicate sample pair from a homogenized bulk soil samples representing one of five soils typical of the eastern United States were placed randomly in the sample batch).

The composition of QC samples were known and the analytical results from each laboratory were required to be compared with the accepted values as the samples are analyzed. This immediate feedback on the functioning of the analytical system allowed analytical and sample processing problems to be resolved quickly, with the result that error from that source was minimized. Six types of QC samples were used in the Northeastern Soil Survey: (1) calibration blanks were used as a check for sample contamination and for baseline drift in the analytical instrument immediately after calibration; (2) reagent blanks underwent the same treatment as the routine samples and served as a check for reagent contamination; (3) QC check samples contained the analyte of interest in the mid-calibration range and served as a check on the accuracy and consistency of the calibration of the instrument throughout the analysis of the sample batch; (4) detection limit QC check samples were low concentration samples that eliminated the necessity of determining the detection limit every day and allowed accuracy to be determined at the low end of the calibration range; (5) matrix spikes were sample aliquots to which known quantities of analyte are added for determining the sample matrix effect on analytical measurements; and (6) analytical duplicates were splits of a single sample and were used to estimate analytical within-batch precision.

In addition to the use of QC samples for quality control, two system audits, or on-site evaluations were also conducted, one immediately after award of the contract to the laboratories and the second after sample analysis had begun.

Internal Consistency Checks

An internal consistency computer program provided a meaningful check of routine data by identifying values that differed from the majority of observed values and that might have gone unnoticed had the check not been made. The checks uncovered errors in data entry and transcription as well as errors that occurred on an analytical batch basis. In this study, a correlation approach was used to assess internal consistency in which the coefficients of determination were obtained by performing weighted linear regressions. From the regressions, studentized residuals and DFFITS statistics were calculated to identify extreme data values that could be considered outliers.

Outliers determined by the computer program and representing only about 1 percent of the data, were checked for transcription errors. For a few analyses, a significant number of outliers were present. There were some parameters that did not correlate well with any of the other parameters.

Data Management

The field sampling and analytical data were entered into the Northeastern survey data bases at Oak Ridge National Laboratory in Tennessee. Both data bases progressed through three phases: raw, verified, and validated. The QA staff at the EPA Environmental Monitoring Systems

Laboratory at Las Vegas, Nevada, verified the two data bases. The field sampling data were entered into data sets from specialized forms, visually checked, and frozen as the official raw data base. The analytical data were entered into data sets and visually checked, thereby allowing errors in transcription to be identified corrected. The verification stage was accomplished by a systematic evaluation of completeness and coding accuracy, and flags were used in the data base to note discrepancies. The verified data base was used to assess data for this QA report. The validation stage identified, confirmed, and flagged data values that warrant special attention or caution when used for data analysis.

Results and Discussion

Detectability

The calculated instrument detection limits were less than the contract-required detection limits in the majority of the cases of parameters for which detection limits were established. The DQOs established for detectability were not met for the cation exchange capacity parameters in ammonium chloride and ammonium acetate, aluminum in potassium chloride, total carbon, and total nitrogen. The calculated instrument detection limits were an order of magnitude above the DQOs for the cation exchange parameters.

Precision

The analytical within-batch precision objectives were satisfied for most of the parameters. These included clay, the pH parameters, exchangeable cations, cation exchange capacity and acidity, extractable iron and aluminum, the extractable sulfates and sulfate isotherm parameters, and total carbon, nitrogen, and sulfur. Occasionally, an objective was not met for an upper or lower tier of a parameter. There were some instances where the DQOs were slightly exceeded for these parameters either above or below the knot. The DQOs were not met for total sand and silt, extractable cations in calcium chloride, and sulfate zero isotherm parameters. When the two tiers were pooled over the total concentration range for each of the parameters, a precision index showed that the particle size and extractable cations in calcium chloride did not meet the overall DQOs.

Although no DQOs were set for the preparation laboratory phase, the preparation laboratory within-batch precision also met the DQOs set for analytical within-batch precision for all parameters except sand and silt, calcium and magnesium in ammonium acetate, the two cation exchange capacities, acidity in barium chloride, cations in calcium chloride, extractable sulfate in water, sulfate zero isotherm, and total nitrogen. This indicates that the preparation laboratories performed relatively well in subsampling the bulk samples.

Within-batch imprecision estimates increased, as expected, from analytical to sample preparation to field sampling. The between-batch precision estimates were generally low.

Accuracy (Interlaboratory Differences)

The Scheffe's pair-wise multiple comparison test showed that about 5 percent of the interlaboratory differences were significantly different and 0.8 percent were highly significantly different. The latter could be considered to be of concern to the data user. Highly significant differences were shown mostly for the cations in calcium chloride. About half the cases were in the Bw audit sample.

The lowest interlaboratory differences were shown for pH and the highest differences were shown for the cation exchange capacity parameters, calcium in calcium chloride, and cations in ammonium chloride. The mean interlaboratory differences for laboratories 1,2,3, and 4 were 9.5, 9.3, 11.6, and 6.9 percent, respectively.

Among the audit samples, the laboratories showed the highest differences overall for the C horizon audit sample and the lowest differences for the A audit sample. The mean interlaboratory differences for the Oa, A, Bs, Bw, and C audit samples were 13.8, 9.3, 14.5, 10.7, and 15.8 percent, respectively.

No single laboratory was consistently superior to the others for all parameters or parameter groups regarding low differences. Each laboratory appears to have individual strengths for specific analytical methods. This is probably a reflection of the combination of experience, instrumentation, and laboratory management practices within each laboratory. This resulted in a patchwork of differences on a parameter group basis.

Representativeness

The field duplicates were representative of the range of concentration in the range of the routine samples for most parameters. The natural audit samples and the preparation duplicates were rarely representative of the routine samples. The preparation duplicates consistently represented only the extreme lower range of routine sample concentrations for a given parameter. The preparation laboratory personnel apparently selected bulk samples for duplication based not on random selection but on the quantity of each sample available. The sampling crews were able to collect the largest amount of sample from the thicker horizons normally found in the lower portion of the soil pedon. Horizon type selection appears to been highly skewed (73 percent) toward the transitional B and C horizons which typically have very low analyte concentrations in their extractions.

Completeness

Ninety-six percent of the designated pedons were sampled. Although this does not fully satisfy the DQO of 100 percent for sampling completeness, a sufficient number of pedons were sampled to enable estimates and conclusions to be drawn from the data. The requested soil sampling and sample processing tasks were performed on 100 percent of the samples received by the preparation laboratory which satisfies the DQO of 100 percent. The analytical completeness level exceeded 99 percent for all parameters. Sufficient data were generated to make conclusions for each parameter in the data bases, with the possible exception of iron in the calcium chloride extract.

Comparability

The verified data bases were used for the assessment of data quality for both the Northeastern and the Southern Blue Ridge Province soil surveys. The data bases from each survey therefore can be compared to each other. Flags were applied consistently.

Sufficient audit sample data were available from the DDRP contract laboratory analyses to provide an estimate of the audit sample composition for use in the assessment of precision, interlaboratory differences, and comparability. Data from each audit sample can be compared between the two surveys for any given parameter. Significant differences can thus be attributed to differing amounts of measurement error. Reanalyses have corrected all data significantly affected by methods amendments which occurred as the survey progressed.

Identical soil preparation methods were used in preparing soil samples for the two surveys. The procedure for selecting the preparation duplicate was refined for the Southern Blue Ridge survey, resulting in better representativeness of the preparation duplicate.

Due to an inconsistent application in the sampling of the field duplicates in the Northeastern survey, the variances for the field duplicates tended to fluctuate among the pedons. Overall within-batch variability was greater in the Southern Blue Ridge survey than in the Northeastern survey. This suggests that the measurement error in the Northeastern survey may have been somewhat underestimated. However, it does not mean that the routine data between regions are not comparable. The same methodology was used in the routine soil sampling for each survey. There were no deviations from the sampling protocols that would compromise the integrity of the routine data. These field sampling discrepancies that could affect data comparability were documented during the Northeastern survey and were resolved. The field sampling audit team did not report any deviations from the sampling protocols that would compromise the integrity of the routine data for the Southern Blue Ridge Province Soil Survey.

As part of the DDRP, an interlaboratory methods comparison study was conducted which compared the analysis of soils for two laboratories using the DDRP methods to 16 statistically chosen external laboratories. These laboratories used their own methods which were similar, but not identical to, the DDRP methods. The results of the study will show the comparability of the DDRP data with other similar surveys using other laboratories.

Conclusions and Recommendations

Analysis of data from the Northeastern Soil Survey indicate areas where improvement is needed in the QA program. The quality assurance data are presented in a manner considered to be the most appropriate for use by the primary data users. The development of this approach resulted from regular interactions with the data users. In addition, the statistical approaches taken and the formats used were assessed in depth by several external reviewers to ensure agreement in the final presentations. A great deal of information is included in the many figures and tables. Each user has a subjective conception for data quality as well as a need for a specific level of data quality desired for his/her own use. The user is therefore encouraged to become familiar in detail with the text, figures, and tables in order to best assess the data for his/her specific needs.

A computerized data entry and verification system should be developed that will calculate the final data values and produce a list of flags and data entry errors. A computer link between the laboratories and the quality assurance staff should be established that will enable the transfer of preliminary and final data. The verification program should be designed to evaluate the quality control checks and other contractual requirements, thereby inducing the laboratories to assume much of the responsibility for identification and correction of errant data. Evaluation of the blind audit samples should be made part of the computer verification system and a better procedure for checking these values be developed. The internal consistency checks should become an integral part of the verification process.

Attention should be given to improving detectability in future surveys. Both instrument detection and system detection limits be should be addressed in the data quality objectives for future surveys.

The DQOs for total sand and total silt should be increased from 1.0 percent to 3.0 percent. A two-tiered precision objective should be defined for the extractable cations in calcium chloride. Specific data quality objectives should be defined for system-wide measurement.

Low concentration audit samples, entered into the system during the sampling phase, should be utilized as substitutes for soil blank samples. A quality control soil audit sample should be incorporated into the quality assurance program to better monitor the analytical results of the laboratories. the laboratories should be required to report the analytical results of the analyses on a batch-by-batch basis to the QA staff immediately after the analysis of each batch. The laboratory protocols should specify a statistically valid method for selecting the preparation duplicate.

An effort should be made to locate an uncontaminated filter material for the determination of the basic cations or modify the pretreatment procedure for the filter material used. Additional methods details should be reviewed and provided where appropriate in order to reduce within-laboratory analytical variability.

The DDRP staff should consider the possibility of choosing laboratories to perform analyses on a parameter basis for those parameters or parameter groups that revealed inherently high differences or where specialized instrumentation is used, e.g., total carbon, nitrogen, and sulfur. A more stringent laboratory selection procedure should be adopted in the pre-evaluation process for the selection of contract laboratories.

The issue of accuracy should be addressed because the current approach using interlaboratory differences has limited utility. Data quality objectives for accuracy should be established.

Section 1

Introduction

Overview of the Direct/Delayed Response Project

The Direct/Delayed Response Project (DDRP) is an integral part of the Aquatic Effects Research Program (AERP) of the U.S. Environmental Protection Agency (EPA). The AERP is conducted under the federally mandated National Acid Precipitation Assessment Program which addresses the concern over potential acidification of surface waters by atmospheric deposition within the United States. The DDRP is administered by the EPA Environmental Research Laboratory in Corvallis, Oregon (ERL-C).

The overall purpose of the DDRP is to characterize geographic regions of the United States as to the predicted relative response of watersheds and surface waters to acidic deposition. The DDRP has been designed under the concept of regionalized integrative surveys which initially is approached from a large region of interest and leads to the selection and study of regionally characteristic systems. These systems can be assessed through detailed, process-oriented research which will aid in the understanding of the underlying mechanisms responsible for observed effects. The projected responses of watershed systems typical of the regional population can then be extrapolated to a larger regional or national scale.

The EPA is assessing the role that atmospheric deposition of sulfur plays in controlling long-term acidification of surface waters (U.S. EPA, 1985*). Recent trend analyses have indicated that the rate of sulfur deposition is slowly declining in the northeastern United States but is increasing in the southeastern United States. If a "direct" response exists between increasing sulfur deposition and decreasing surface water alkalinity, then the negative impact of current effects on surface water probably would increase with increasing levels of deposition. Conditions would improve as the levels of deposition decline. If surface water chemistry changes in a "delayed" manner, e.g., due to chemical changes in the watershed, then future changes in surface water chemistry (even with stable or declining rates of deposition) become difficult to predict. This range of potential effects has significant implications to public policy decisions on sulfur emissions control strategies.

Specific objectives of DDRP are to (1) define physical, chemical, and mineralogical characteristics of the soils across these regions, (2) assess the variability of these characteristics, (3) determine which of these characteristics are most strongly related to surface water chemistry, (4) estimate the relative importance of key watershed processes in controlling surface water chemistry across the regions of concern, and (5) classify the sample of watersheds with regard to their response to sulfur deposition and extrapolate the results from the sample of watersheds to the regions of concern.

A variety of data sources and methods of analysis will be used to address the objectives of DDRP. In addition to the data collected during DDRP, other data sources include the following:

- National Surface Water Survey (NSWS) [water chemistry data]
- Acid Deposition Data Network (ADDNET), including GEOECOLOGY

[atmospheric precipitation chemistry data]

- Soil Conservation Service (SCS) Soils-5 [soil physical and chemical data]
- Adirondack Watershed [whole watershed chemistry data]
- Acid Deposition System (ADS) [total sulfur deposition data]
- U.S. Geological Survey [runoff data]

Also, data from EPA long-term monitoring sites, episodic event monitoring sites, and intensively studied watersheds will be used in the data analysis.

The data that are collected will be analyzed at three levels:

- Level I - System description and statistical analysis
- Level II - Single factor response-time estimates
- Level III - Dynamic systems modeling

Field and laboratory data collected in DDRP are included in the Level I system description. Next, these data are used in Level II to develop single factor estimates of the response time of watershed properties, e.g., sulfate adsorption capacity, to acidic deposition. The detailed data from special interest watersheds are used in Level III to calibrate three dynamic simulation models, MAGIC (Cosby et al., 1984), ILWAS (Chen et al., 1984), and Trickle-Down (Schnoor et al., 1984), that predict regional responses to acidic deposition.

Northeastern Soil Survey

The northeastern region of the United States was selected for study because of its suspected sensitivity to acidic deposition. The focus was on regionally representative watersheds that are potentially sensitive to acidic deposition and that exhibit a wide contrast in soil and watershed characteristics and in levels of deposition. The Northeastern Soil Survey focused on a large geographic area encompassing the states of Maine, New Hampshire, Vermont, New York, Massachusetts, Connecticut, Rhode Island, and the northern portion of Pennsylvania.

The soil sampling task leader at ERL-C had overall responsibility for the soil mapping and sampling, including quality assurance/ quality control (QA/QC) for site selection, pedon characterization, and collection of bulk samples and clods. Analytical and sampling methods, QA/QC procedures, logistical support, and analytical services were provided by the EPA, Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV). There were 14 sampling crews, each consisting of three to four soil scientists, involved in the sampling phase of the northeastern region. In addition to collecting 5.5-kilogram routine soil samples, each sampling crew collected one duplicate sample per day for QA purposes. Details of the soil mapping and sampling are contained in a separate QA report (Coffey et al., 1987).

As part of the DDRP, four preparation laboratories were established in the northeastern region of the United States to process soil samples collected by the sampling crews and to perform preliminary analyses on these samples. The preparation laboratories were located within the soil science departments at the following land grant universities:

- University of Massachusetts, Amherst, Massachusetts
- University of Connecticut, Storrs, Connecticut
- University of Maine, Orono, Maine
- Cornell University, Ithaca, New York

The handling of soil samples at each preparation laboratory is discussed in a separate QA report (Papp and Van Remortel, 1987). Bulk samples were processed, homogenized, and subsampled. Air-dry moisture content and percent rock fragments in the 2- to 20-millimeter fraction, and inorganic carbon were determined. The presence of inorganic carbon was estimated by the effervescence test. In addition, the bulk density of replicate soil clods was determined. One kilogram samples were prepared from the homogenized air-dry bulk soil samples. The analytical samples were grouped into batches and were randomized within each batch. Field duplicates, natural audit samples from EMSL-LV, and a preparation duplicate were placed in each batch for QA purposes. The batches were distibuted to four analytical laboratories contracted by EPA.

The QA/QC measures were applied in order to maintain consistency in the soil protocols for field sampling, sample preparation, and sample analysis. These protocols ensured that the soil sample analyses would yield analytical data of known quality. The sampling crews and preparation laboratory personnel received training on their respective activities. The QA staff from EMSL-LV and ERL-C conducted on-site systems audits of the sampling crews, preparation laboratories, and contract analytical laboratories. Weekly communication between QA personnel and laboratory personnel was established to identify, discuss, and resolve issues. Survey participants attended an exit meeting held in Las Vegas, Nevada, in January, 1986. The purposes of the meeting were to review the mapping, sampling, and preparation activities and generate suggestions for future surveys.

The design of the QA program affects the ultimate quality of data derived from physical, chemical, and mineralogical analyses of the soil samples. The quality of the data enables potential users to determine if the data meet their specific needs. In addition, the QA program was conceived as a means to ensure that the data are comparable within and across the regions of concern. Soils were described and sampled according to documented protocols (Blume et al., 1987). Contract Laboratory analyses also were conducted according to documented protocols (Cappo et al., 1987) by four contract laboratories.

Mineralogical analyses were performed on about 10 percent of the routine samples. Semiquantitative X-ray diffraction and X-ray fluorescence data will be included in a forthcoming report (Schumacher et al., in preparation).

Organization of the Report

This document has been organized into four main sections. The first section provides an overview of DDRP objectives and the Northeastern Soil Survey analytical data base. The second section addresses the overall QA program, its relation to data quality assessment, and the use of QA/QC samples during the various stages of data collection. The third section provides results and discussion concerning the QA data analysis and the internal verification checks for nine parameter groups. The fourth section addresses the conclusions and recommendations that have been generated from these findings, particularly in regard to issues of concern, improvement in QA design, and preparation for QA efforts in the DDRP Mid-Appalachian Soil Survey and other future surveys.

Data quality is discussed in terms of detectability, precision, accuracy (interlaboratory differences), representativeness, completeness, and comparability. The relationship of data quality achievements to the data quality objectives (DQOs) established at the beginning of the program is evaluated.

Description of Parameter Groups

The DDRP QA staff organized the 51 analytical parameters into nine groups and subsequently evaluated each group independently according to the DQOs specified for the Northeastern survey. The nine parameter groups are briefly summarized below:

1. Moisture, Specific Surface, and Particle Size (twelve parameters)--The air-dry soil moisture content is determined in order to place all subsequent aliquots on an oven-dry weight basis. Specific surface is measured in mineral soils using a gravimetric saturation method and is correlated with data for cation exchange capacity, sulfate adsorption and desorption, and clay mineralogy. Particle size analysis is performed on the less than 2-millimeter size fractions of mineral soils for characterization and classification purposes.

2. Soil pH (three parameters)--The pH is a measure of free hydrogen ion activity expressed as the negative logarithm. The pH measurements are determined in three soil suspensions: deionized water, 0.002M calcium chloride, and 0.01M calcium chloride. The method for pH in deionized water is universally used in soil laboratories. The two methods for pH in 0.002M and 0.01M $CaCl_2$ are

widely used to reflect the salt effect which occurs naturally in soils.

3. Exchangeable Cations in Ammonium Chloride (four parameters)--The exchangeable cations (calcium, magnesium, potassium, and sodium) are extracted during the cation exchange capacity (CEC) determinations and can be used to calculate the percent base saturation of the soil and to define selectivity coefficients and cation pools for the DDRP models.

4. Exchangeable Cations in Ammonium Acetate (four parameters)--The exchangeable cations (calcium, magnesium, potassium, and sodium) are extracted during the CEC determinations and can be used to calculate the percent base saturation of the soil and to define selectivity coefficients and cation pools for the DDRP models.

5. Cation Exchange Capacity and Exchangeable Acidity (five parameters)--The CEC indicates the ability of a soil to adsorb cations, especially the exchangeable basic cations mentioned above. The CEC is highly correlated with the buffering capacity of the soil. Two saturating solutions for the exchangeable cation component of CEC are used: buffered ammonium acetate solution as the cation component of "total" CEC and neutral ammonium chloride solution as the cation component of "effective" CEC. Exchangeable acidity is a measure of the exchangeable acidic cations, i.e., hydrogen and aluminum, that are held on a soil particle surface, in contrast to the active acidity of these cations in solution. Two methods of analysis for acidity are used: a buffered barium chloride triethanolamine extraction and a neutral potassium chloride extraction. The first method is a back-titration which indicates "total" exchangeable acidity, including aluminum. The second method is a direct titration which estimates "effective" exchangeable acidity. Exchangeable aluminum was also determined in potassium chloride.

6. Extractable Cations in Calcium Chloride (six parameters)--Lime potential [pH - 1/2 pCa] is used as an input for certain predictive models. Aluminum potential [3pH - pAl] is another important characteristic for watershed modeling. The soil is extracted with 0.002M calcium chloride and analyzed for calcium and aluminum concentrations. The magnesium, potassium, sodium, and iron concentrations also are determined and are compared to cation concentrations in other extracts.

7. Extractable Iron and Aluminum (six parameters)--Sulfate adsorption is highly correlated with the presence of iron and aluminum. Each of three extractions yields an estimate of a specific iron or aluminum fraction: sodium pyrophosphate estimates organic iron and aluminum; acid oxalate estimates organic iron and aluminum plus sesquioxides; and citrate-dithionite estimates nonsilicate iron and aluminum.

8. Extractable Sulfate and Sulfate Adsorption Isotherms (eight parameters)--Sulfate is determined in two different extracts: deionized water, which estimates loosely-bound sulfate; and 500 mg P/L as sodium phosphate, which estimates the readily extractable sulfate on the anion exchange sites. The ability of soil to adsorb sulfate is related to anion adsorption capacity. Isotherms are developed by placing soil samples in six magnesium sulfate solutions of different concentrations: 0, 2, 4, 8, 16, and 32 mg S/L. A determination is made of the amount of sulfate remaining in solution after one-hour contact with the soil and subtraction yields the net sulfate sorption. The isotherms represent the maximum sulfate adsorption of the soil under laboratory conditions and are used to predict changes in sorbed and dissolved sulfate as a result of altered deposition.

9. Total Carbon, Nitrogen, and Sulfur (three parameters)--Total carbon and nitrogen are closely related to the type and amount of soil organic matter. Total sulfur is used as a benchmark to monitor future inputs of anthropogenic sulfur.

Description of Parameters

Throughout this document chemical and physical soil parameters are referenced either by a data-variable or descriptive parameter name. A list of parameters and their corresponding descriptions based on a similar presentation in Turner et al. (1989) is given in Table 1-1. The order of the parameters is consistent with their order of presentation in this report.

Table 1-1. Analytical Parameters Measured in the Northeastern Soil Survey

Parameter	Description of Parameter
MOIST	Percent air-dry soil moisture measured at the analytical laboratory and expressed as a percentage on an oven-dry weight basis. Mineral soils were dried at 105°C, organic soils at 60°C.
SP_SUR	Specific surface area determined by a gravimetric method of saturation with ethylene glycol monoethyl ether (EGME).
SAND	Total sand is the portion of the sample with particle diameter between 0.05 mm and 2.0 mm. It was calculated as the summation of percentages for individual sand fractions: VCOS + COS + MS + FS + VFS.
VCOS	Very coarse sand is the sand fraction between 1.0 mm and 2.0 mm. It was determined by sieving the sand which had been separated from the silt and clay.
COS	Coarse sand is the sand fraction between 0.5 mm and 1.0 mm. It was determined by sieving the sand which had been separated from the silt and clay.
MS	Medium sand is the sand fraction between 0.25 mm and 0.50 mm. It was determined by sieving the sand which had been separated from the silt and clay.
FS	Fine sand is the sand fraction between 0.10 mm and 0.25 mm. It was determined by sieving the sand which had been separated from the silt and clay.
VFS	Very fine sand is the sand fraction between 0.05 mm and 0.10 mm. It was determined by sieving the sand which had been separated from the silt and clay.
SILT	Total silt is the portion of the sample with particle diameter between 0.002 mm and 0.05 mm. It was calculated by subtracting from 100 percent the sum of the total sand and clay.
COSI	Coarse silt is the silt fraction between 0.02 mm and 0.05 mm. It was calculated by subtracting the fine silt fraction from the total silt.
FSI	Fine silt is the silt fraction between 0.002 mm and 0.02 mm. It was determined by the pipet method (USDA/SCS, 1984) and was calculated by subtracting the clay fraction from the less than 0.02 mm fraction.
CLAY	Total clay is the portion of the sample with particle diameter of less than 0.002 mm and is determined using the pipet method.
PH_H20	pH determined in a deionized water extract using a 1:1 mineral soil to solution ratio and 1:5 organic soil to solution ratio. The pH was measured with a pH meter and combination electrode.
PH_002M	pH determined in a 0.002M calcium chloride extract using a 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio. The pH was measured with a pH meter and combination electrode.
PH_01M	pH determined in a 0.01M calcium chloride extract using a 1:1 mineral soil to solution ratio and 1:5 organic soil to solution ratio. The pH was measured with a pH meter and combination electrode.
CA_CL	Exchangeable calcium determined with an unbuffered 1M ammonium chloride solution. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
MG_CL	Exchangeable magnesium determined with an unbuffered 1M ammonium chloride solution. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
K_CL	Exchangeable potassium determined with an unbuffered 1M ammonium chloride solution. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry was specified.
NA_CL	Exchangeable sodium determined with an unbuffered 1M ammonium chloride solution. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
CA_OAC	Exchangeable calcium determined with 1M ammonium acetate solution buffered at pH 7.0. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.

(continued)

Table 1-1. Continued

Parameter	Description of Parameter
MG_OAC	Exchangeable magnesium determined with 1M ammonium acetate solution buffered at pH 7.0. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
K_OAC	Exchangeable potassium determined with 1M ammonium acetate solution buffered at pH 7.0. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry was specified.
NA_OAC	Exchangeable sodium determined with 1M ammonium acetate solution buffered at pH 7.0. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
CEC_CL	Cation exchange capacity determined with an unbuffered 1M ammonium chloride solution is the effective CEC which occurs at approximately the field pH when combined with the acidity component. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Samples were analyzed for ammonium content by one of three methods: automated distillation/titration; manual distillation/automated titration; or ammonium displacement/flow injection analysis.
CEC_OAC	Cation exchange capacity determined with 1M ammonium acetate solution buffered at pH 7.0 is the theoretical estimate of the maximum potential CEC for a specific soil when combined with the acidity component. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Samples were analyzed for ammonium content by one of three methods: automated distillation/titration; manual distillation/automated titration; or ammonium displacement/flow injection analysis.
AC_KCL	Effective exchangeable acidity determined by titration in an unbuffered 1M potassium chloride extraction using a 1:20 soil to solution ratio.
AC_BACL	Total exchangeable acidity determined by titration in a buffered (pH 8.2) barium chloride triethanolamine extraction using a 1:30 soil to solution ratio.
AL_KCL	Extractable aluminum determined by an unbuffered 1M potassium chloride extraction using a 1:20 soil to solution ratio. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
CA_CL2	Extractable calcium determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. The calcium is used to calculate lime potential. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
MG_CL2	Extractable magnesium determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
K_CL2	Extractable potassium determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. Atomic absorption spectrometry was specified.
NA_CL2	Extractable sodium determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
FE_CL2	Extractable iron determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
AL_CL2	Extractable aluminum determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. The aluminum concentration obtained from this procedure is used to calculate aluminum potential. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
FE_PYP	Extractable iron determined by a 0.1M sodium pyrophosphate extraction using a 1:100 soil to solution ratio. The pyrophosphate extract estimates organically-bound iron. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.

(continued)

Table 1-1. Continued

Parameter	Description of Parameter
AL_PYP	Extractable aluminum determined by a 0.1M sodium pyrophosphate extraction using a 1:100 soil to solution ratio. The pyrophosphate extract estimates organically-bound aluminum. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
FE_AO	Extractable iron determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio. The acid oxalate extract estimates organic and amorphous iron oxides. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
AL_AO	Extractable aluminum determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio. The acid oxalate extract estimates organic and amorphous aluminum oxides. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
FE_CD	Extractable iron determined by a sodium citrate-sodium dithionite extraction using a 1:30 soil to solution ratio. The citrate dithionite extract estimates non-silicate iron. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
AL_CD	Extractable aluminum determined by a sodium citrate-sodium dithionite extraction using a 1:30 soil to solution ratio. The citrate dithionite extract estimates non-silicate aluminum. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
SO4_H2O	Extractable sulfate determined with a double deionized water extract. This extraction approximates the sulfate which will readily enter the soil solution and uses a 1:20 soil to solution ratio. Ion chromatography was specified.
SO4_PO4	Extractable sulfate determined with a 0.016M sodium phosphate (500 mg P/L) extract. This extraction approximates the total amount of adsorbed sulfate and uses a 1:20 soil to solution ratio. Ion chromatography was specified.
SO4_0	Sulfate remaining in a 0 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_2	Sulfate remaining in a 2 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_4	Sulfate remaining in a 4 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_8	Sulfate remaining in a 8 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_16	Sulfate remaining in a 16 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_32	Sulfate remaining in a 32 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
C_TOT	Total carbon determined by rapid oxidation followed by thermal conductivity detection using an automated CHN analyzer. Total carbon can be used to characterize the amount of organic material in the soil.
N_TOT	Total nitrogen determined by rapid oxidation followed by thermal conductivity detection using an automated CHN analyzer. Total nitrogen can be used to characterize the organic material in the soil.
S_TOT	Total sulfur determined by automated sample combustion followed by infrared detection or titration of evolved sulfur dioxide.

Section 2

Quality Assurance Program

Quality assurance has been defined as "those operations and procedures which are undertaken to provide measurement data of stated quality with a stated probability of being right" (Taylor, 1987). The QA/QC procedures for the Northeastern survey were designed to ensure that the best possible data were collected and that the quality of the data could be evaluated and documented. These procedures included the preparation of written protocols and manuals describing: (1) soil sampling, preparation and analysis, (2) application of QA/QC during field and laboratory activities, and (3) verification of the descriptive and analytical data. The protocols were tested and implemented in the survey. Specific aspects of the QA program are described in the following subsections.

Selection of Analytical Laboratories

Specifications for the laboratory analyses were defined during the initial development of the QA program. The estimated number of samples to be analyzed and the schedule of sample collection were defined during logistics planning. The Contract Laboratory Program (CLP) already had been established to support the hazardous waste remediation activities of EPA and no single EPA laboratory had the analytical capabilities or resources to provide the required analytical services. Hence, these services were obtained through solicitations with commercial analytical laboratories. The use of multiple analytical laboratories, however, required that the selection and documentation of analytical methods and QA activities had to be carefully implemented and monitored to ensure consistent and adequate performance in all laboratories. The contracting process involved the following activities:

- preparation of a detailed statement of work (SOW) which defined the analytical and QA/QC requirements in a contractual format
- preparation and advertisement of an invitation for bid (IFB) to solicit analytical support
- evaluation of all bidders within a competitive range followed by selection of qualified laboratories

Statement of Work

Monitoring of data quality at each contractor analytical laboratory was necessary in order to minimize data variability both within and among the laboratories. Although the DDRP Analytical Methods Manual (Cappo et al., 1987) and the DDRP QA Plan (Bartz et al., 1987) were drafted in the early phases of the planning process, the methods and QA/QC requirements had to be restructured in a SOW in order to obtain support services. This involved careful review of the analytical and logistical requirements, i.e., reporting and QC stipulations, to ensure their clarity in the SOW and their ability to be satisfied according to contract specifications. The primary administrative protocols in the SOW were as follows:

- A contractor could bid on the analysis of one or more bid lots (600 samples per bid lot) that would be delivered to the analytical laboratory at a maximum rate of 60 samples per week, grouped in batches of 60 samples per batch.
- Delivery of the completed data package by the contractor was required

within 60 days of sample receipt for Solicitation #1, and within 45 days of sample receipt for Solicitation #2. An incentive for early delivery of data and a consideration for late delivery of data were established.

- Failure of the contractor to provide deliverables as required by the SOW resulted in up to 15 percent of the sample price initially withheld. All four of the analytical laboratories eventually were paid the entire 15 percent withholding after the data were verified and any confirmation/reanalysis requests were serviced.

The analytical laboratories were required to follow the methods exactly as specified in the SOW. The project officer was authorized to provide technical clarifications for the contractor laboratory, but contractual changes were made only with the written approval of the EPA contract officer.

Performance Evaluations

The IFB was advertised in the *Commerce Business Daily*. All interested laboratories received a set of pre-award performance evaluation (PE) samples as the next step in the selection qualification. These laboratories were required to analyze the PE samples and to report results within 25 days after receipt of sample. The PE samples were intended to represent soil samples at both the low and high analyte concentrations expected for the survey. Data packages received from each laboratory were evaluated and graded on the accuracy of analytical data as well as the quality and completeness of the data package using the scoring sheet provided in the DDRP QA Plan (Bartz et al., 1987). This procedure identified those laboratories that could not successfully perform the analytical tasks.

All laboratories successfully passing the PE sample evaluation were visited by EPA representatives in order to verify the qualifications and capabilities of these laboratories to meet the contractual requirements. The EPA team determined whether each analytical laboratory had adequate facilities, equipment, personnel, and technical capabilities to analyze samples in accordance with the SOW. These visits also provided an opportunity to clarify contractual specifications with laboratory personnel and to identify deficiencies that were observed during the PE phase.

Five laboratories successfully passed both the performance and on-site evaluations and were awarded contracts to provide analytical services for the Northeastern survey. Later, however, during the routine analysis of samples, it was determined that one of the laboratories could not maintain the specified level of quality in the analyses and this laboratory was disqualified. The remaining samples in archive were retrieved by EMSL-LV and were redistributed to two of the other four laboratories for analysis. All data from the disqualified fifth laboratory have been removed from the DDRP data bases.

Contract Solicitations

The analytical methods and associated QA/QC protocols that were used in the Northeastern survey were selected so that the DDRP data could be compared with other similar data bases, e.g., the DDRP Southern Blue Ridge Province survey data base. On-site system audits ensured that the laboratory procedures were followed correctly. Differences in methodology and reporting units occurred among the three contract solicitations. These differences were rectified as a result of the on-site system audit. The distribution of batches among the laboratories, by solicitation, is outlined in Table 2-1.

Prior to beginning of routine sample analysis, the original contract solicitation containing the analytical methodology was employed in the analysis of audit sample data from three referee laboratories. This solicitation was modified to clarify the handling of organic samples and served as the basis for Solicitation #2. Thirty batches, encompassing about half of the samples, were analyzed at this time.

Solicitation #2 differed from Solicitation #1 primarily in the data reporting format, the contract-required detection limits (CRDLs), as presented in Table 2-2, and two minor changes in method procedures. Solicitation #1 did not require the laboratories to report raw data or blank-corrected data, whereas Solicitation #2 supplied forms for the reporting of both types of data. The CRDLs in Solicitation #2 were

Table 2-1. Distribution of Batches by Contract Solicitation and Laboratory

Solicitation/ Laboratory	Number of Batches	Batch numbers
S1 / L2[a]	14	10102, 10106, 10110, 10112, 10401, 10402, 10403, 10404, 10405, 10406, 10407, 10410, 10413, 10504
S1 / L4[a]	15	10201, 10202, 10203, 10205, 10206, 10209, 10210, 10214, 10215, 10301, 10302, 10303, 10304, 10305, 10411
S2 / L1	15	10101, 10103, 10104, 10105, 10107, 10108, 10109, 10111, 10113, 10114, 10211, 10412, 10501, 10502, 10503
S2 / L3	4	10409, 10414, 10416, 10417
S3 / L1[b]	4	19204, 19208, 19408, 19505
S3 / L2[a,b]	4	19207, 19212, 19213, 19415

[a] Laboratories 2 and 4 reanalyzed the cation parameters under Solicitation #3.

[b] Reanalysis solicitation for batches from disqualified laboratory.

lowered for calcium, magnesium, potassium, and sodium. Establishing the CRDLs for each of the various parameters for the audit soil samples was greatly influenced by analyte concentration in the soil, and laboratory analytical capability. The CRDLs in the first solicitation for the basic cations were inadvertently set higher than those concentrations which occurred naturally in the soils. In addition, the laboratories had the capability of determining lower analyte concentrations in the soils than required by the CRDLs. Subsequently, the CRDLs were lowered for Solicitation #2. The two method changes that occurred were: (1) the soil-to-solution ratio changed from 1:1 to 1:2 for PH_002M, bringing data for this parameter into conformity with the cations in calcium chloride, and (2) the acidification step for AL_KCL was placed before the titration step for AC_KCL. For the sake of comparability, all samples were reanalyzed for the parameters stated. About half of the soil samples were analyzed under Solicitation #1 and the other half under Solicitation #2.

One of the five analytical laboratories originally selected was eventually disqualified. Therefore, a third solicitation was initiated to allow two of the other laboratories to analyse the samples that were retrieved from the disqualified laboratory. The principal changes in specifications for Solicitation #3 were the additional lowering of CRDLs for the cation analyses (see Table 2-2) and the removal of a dilution step for SO4_PO4. Reanalysis of the affected parameters was performed on all previous samples at EPA expense. Certain samples among those retrieved underwent additional processing at EMSL-LV in order to prepare them for analysis, as outlined in Table 2-3. The additional processing involved rehomogenization of the soil sample by riffle splitting. This was required in order to ensure that all retrieved samples would be homogenous when submitted to the laboratories chosen for the reanalysis. Sample reanalyses

Table 2-2. Contract-Required Detection Limits for Contract Solicitations

Parameter	Solicitation		
	1	2	3
CA_CL, CA_OAC, CA_CL2[a]	1.00 mg/L	0.20 mg/L	0.05 mg/L
MG_CL, MG_OAC, MG_CL2	1.00 mg/L	0.20 mg/L	0.05 mg/L
K_CL, K_OAC, K_CL2	1.00 mg/L	0.20 mg/L	0.05 mg/L
NA_CL, NA_OAC, NA_CL2	1.00 mg/L	0.20 mg/L	0.05 mg/L
CEC_CL, CEC_OAC	0.20 meq/L	0.01 meq/L	0.01 meq[b]
AC_KCL	0.75 meq/L	0.25 meq/L	0.25 meq
AC_BACL	0.02 meq/L	0.40 meq/L	0.40 meq
AL_KCL	0.50 mg/L	0.50 mg/L	0.10 mg/L
FE_CL2, AL_CL2	0.50 mg/L	0.50 mg/L	0.05 mg/L
FE_PYP, FE_AO, FE_CD	0.50 mg/L	0.50 mg/L	0.50 mg/L
AL_PYP, AL_AO, AL_CD	0.50 mg/L	0.50 mg/L	0.50 mg/L
SO4_H2O, SO4_PO4, SO4_0-32	0.1 mg SO_4/L	0.10 mg SO_4/L	0.10 mg S/L
C_TOT, N_TOT	0.005 wt%	0.005 wt%	0.010 wt%
S_TOT	0.010 wt%	0.010 wt%	0.010 wt%

[a] CRDL for CA_CL2 reported as standard deviation of ten nonconsecutive blanks

[b] meq for distillation/titration analysis and meq/L for flow injection analysis

Table 2-3. Soil Samples For Secondary Processing Following Retrieval From Disqualified Analytical Laboratory

Batch number	Sample numbers
19204	All except 3, 8, 9, 11, 30, 41, 43, and 44
19207	All except 4, 7, 9, 14, 40, 43, and 44
19208	All except 2, 26, 29, 32, 33, 41, 43, and 44
19212	All except 2, 8, 9, 14, 22, 24, 32, 43, and 44
19213	All except 13, 14, 20, 34, 43, and 44
19408	All except 10, 19, 27, 28, 33, 34, 42, and 43
19415	All except 2, 3, 5, 7, 8, 12, 13, 14, 15, 17, 18, 27, 29, 31, 33, 34, 36, 40, 41, 42, 43, and 44
19505	All except 1, 9, 13, 21, 22, 31, 35, 36, 38, 43, and 44

have corrected all data affected by methods changes which occurred as the DDRP surveys progressed.

An international interlaboratory comparability study has been completed using DDRP soil audit samples to compare data from the DDRP analytical methods to data from other methods currently in use at soil characterization laboratories throughout the United States and Canada. Results from this study will be summarized in a forthcoming report (Fenstermaker et al., in preparation).

Analytical Laboratory Operations

Data Reporting

All samples received at the analytical laboratory were checked in by a receiving clerk who: (1) recorded on the shipping form the date the samples were received, (2) checked the integrity of the samples, (3) checked the sample labels to identify discrepancies on the shipping form, and (4) sent copies of the shipping form to the EPA Sample Management Office in Washington, D. C. and to the QA staff at EMSL-LV. If there were any discrepancies or problems such as sample leakage or insufficient sample volume, the QA manager was notified immediately for instructions. The samples were refrigerated at 4 °C as soon as possible after receipt by the laboratory and were kept under refrigeration when not in use. After all analyses were completed and the results were checked, the samples were placed in longer-term cold storage in case reanalysis was requested.

Analytical data were reported according to the protocols specified in the DDRP Analytical Methods Manual (Cappo et al., 1987). After each sample was completely analyzed, the results were entered on summary data forms. Where appropriate, the data were annotated with the data qualifiers, or flags, listed in Appendix A. The raw data were reported on separate data forms for the second half of the survey. The laboratory managers signed each completed form to indicate that the data had been reviewed and that the samples were analyzed exactly as described in the SOW. Each manager was responsible for documenting any deviations from the SOW. An index of the data forms used by the analytical laboratories is provided in Appendix B.

Copies of the raw data were submitted upon request of the QA manager; otherwise all original raw data were retained at the analytical laboratories. The raw data include data system printouts, chromatograms, notebooks, individual data sheets, and QC charts.

System Audits

Each analytical laboratory underwent a minimum of two system audits, i.e., on-site evaluations. The first audit was performed after the laboratory had successfully analyzed the set of pre-award PE samples or, occasionally, during the PE sample analyses. The QA manager or authorized representative evaluated each of the laboratory functions that were pertinent to the analyses. A questionnaire was used to assist in this evaluation (see example in Bartz et al., 1987). The auditor summarized all observations in an audit report and brought any discrepancies to the attention of the laboratory manager.

The second on-site audit was conducted after sample analyses had begun. The evaluation questionnaire was completed with emphasis on all changes occurring since the first audit. Data from the audit sample pairs and QC samples received to date were reviewed. An audit report was written for this and any subsequent on-site evaluations.

Daily communication was maintained between the QA staff and designated laboratory personnel during the periods when samples were being analyzed. The objectives of daily communication were to assure that each laboratory was satisfying the QC requirements and to obtain a preliminary evaluation of data quality and laboratory performance. This enabled the QA auditors to become familiar with analytical difficulties and with preliminary data. Thus, verification of the data was underway prior to receipt of the data package by the QA staff.

Laboratory Protocols

General laboratory QC protocols included the use of suitable laboratory facilities, appropriate instrumentation with documented performance characteristics, reagents and labware of sufficient quality and quantity for the specific purpose, and adequately trained personnel. Documentation of the standard operating procedures of the laboratory, a list of in-house samples, and up-to-date QC charts were required. The laboratories were not required to use specific makes or models of instruments, although recommendations were given.

The analytical instruments for all of the methods required some form of calibration. For most methods, a series of standards were analyzed and a calibration curve was derived each time samples were analyzed. The range of analyte concentrations in the calibration standards was required to bracket the expected analyte concentrations in the routine samples without exceeding the linear dynamic range of the instrument. This range was determined by a least squares regression analysis (Steel and Torrie, 1960), with a correlation requirement for concentration versus instrument response of 0.99 or greater.

Quality Assurance and Quality Control Samples

The QA samples were used for independently assessing data quality and for monitoring the internal QC procedures. QA samples differ from QC samples in that they are submitted as blind samples to the laboratories, i.e., their identity and composition are unknown to the analyst. Data quality assessment is undertaken in statistical terms and is accomplished by the inclusion of replicate (usually duplicate) samples with the routine samples for analysis.

The QC samples were used to reduce random and systematic errors, and to maintain specified tolerable limits. These samples were created and used by the laboratories to evaluate the calibration and standardization of instruments and to identify problems such as contamination or analytical interference.

Description of Quality Assurance Samples

Three types of QA samples were used in the Northeastern survey:

- field duplicates,
- preparation duplicates,
- natural audit samples.

The number and percentage of QA and routine samples used for the data quality assessment are shown in Table 2-4.

Table 2-4. Quality Assurance and Routine Samples Used in the Northeastern Soil Survey

Sample type	Number of samples	Percent of total
QA field	270	13
QA preparation	55	3
QA natural audits	112	5
Routine [a]	1634	79
Total	2,071	

[a] Mineral routine 1354 (83% of routine samples)
Organic routine 280 (17% of routine samples)

Field Duplicate Samples

Each sampling crew was required to sample one soil horizon in duplicate per day, collecting alternate portions of soil for each sample (Bartz et al., 1987). One sample was considered to be the routine sample and the other was designated the field duplicate. Since more than one pedon could be sampled on an average day, not every pedon was sampled for a duplicate horizon sample. A total of 270 field duplicates were collected. After processing, the field duplicates were placed randomly with their associated pedon samples in batches of approximately 42 soil samples each.

Certain statistical analyses utilized only the 270 field duplicates, while other analyses used the 270 field duplicate pairs, i.e., the field duplicates in conjunction with their associated routine samples. The distribution of field duplicate pairs among the preparation laboratories and the analytical laboratories is shown in Table 2-5.

Preparation Duplicate Samples

Each preparation laboratory manager chose one routine soil sample per batch and subsampled a duplicate using a Jones-type riffle splitter. Each preparation duplicate was placed randomly within its associated batch. Certain statistical analyses utilized only the 55 preparation duplicates, while other analyses used the 55 preparation duplicate pairs, i.e., the preparation duplicates in conjunction with their associated routine samples. The distribution of preparation duplicate pairs among the analytical laboratories is shown in Table 2-6.

Natural Audit Samples

Bulk soil samples representing five major soil horizons of the eastern United States were collected in multiple 55-gallon drums for use as natural audit samples. The horizons represented by these samples were Oa, A, Bs, Bw, and C. Subsamples from each of these bulk samples were prepared by EMSL-LV staff and were forwarded to the preparation laboratories for direct random placement into the batches at a rate of one pair per batch. These natural audit samples did not undergo any processing at the preparation laboratory. The distribution of the natural audit pairs among the analytical laboratories is presented in Table 2-7.

Sample Flow

The routine and field duplicate samples were collected by 14 sampling crews from each of the selected pedons in the field. A pedon is a three-dimensional body of soil having lateral dimensions large enough (1 to 10 square meters in area) to permit the study of its soil horizons, or horizontal layers. These

Table 2-5. Distribution of Field Duplicate Sample Pairs Among Sampling Crews, Preparation Laboratories, and Analytical Laboratories

Sampling Crew	Analytical laboratory										Total pairs by crew
	1			2			3	4			
	Preparation laboratory[a]										
	MA	ME	NY	MA	ME	NY	NY	MA	CT	NY	
CT01	0	0	0	0	0	0	0	0	23	0	23
MA01	5	0	0	5	0	0	0	12	0	0	22
MA02	6	0	0	13	0	0	0	10	0	0	29
ME01	0	17	0	0	16	0	0	0	0	0	33
ME02	0	19	0	0	0	0	0	0	0	0	19
ME03	0	5	0	0	4	0	0	0	0	0	9
ME04	0	5	0	0	0	0	0	0	0	0	5
NH01	4	0	0	0	0	0	0	11	0	0	15
NH02	0	0	0	0	0	1	0	0	0	0	1
NY01	0	0	0	0	0	19	5	0	0	6	30
NY02	0	0	5	0	0	21	0	0	0	0	26
NY03	0	0	5	0	0	17	6	0	0	0	28
NY04	0	0	0	0	0	2	5	0	0	0	7
PA01	0	0	19	0	0	4	0	0	0	0	23
	Summary of field pairs/among:										
Sampling crews											270
Preparation labs	15	46	29	18	20	64	16	33	23	6	
Analytical labs			90			102	16			62	

[a] MA = Massachusetts, ME = Maine, NY = New York, CT = Connecticut.

Table 2-6. Distribution of Preparation Duplicate Sample Pairs Among Preparation Laboratories and Analytical Laboratories

Analytical laboratory	Preparation laboratory[a] MA	ME	CT	NY	Total pairs
1	3	10	0	6	19
2	3	4	0	11	18
3	0	0	0	4	4
4	9	0	4	1	14
Total pairs	15	14	4	22	55

[a] MA = Massachusetts, ME = Maine, CT = Connecticut, NY = New York.

Table 2-7. Distribution of Natural Audit Pairs Among Analytical Laboratories

Analytical laboratory	Audit sample Oa	A	Bs	Bw	C	Total pairs
1	2	4	2	5	6	19
2	2	4	5	4	3	18
3	0	0	3	1	0	4
4	2	0	5	3	5	15
Total pairs	6	8	15	13	14	56

samples were delivered to four preparation laboratories. The laboratories processed the samples and prepared the preparation duplicates. Batches of soil samples were assembled, each containing field duplicates (two to six per batch, depending on the number of pedons represented in the batch), one preparation duplicate, and one pair of audit samples. The balance of the batch was composed of routine samples from the pedons. The completed batches of approximately 42 samples were distributed among the four contract analytical laboratories for analysis.

Data from the audit samples can be used to evaluate within-batch precision and analytical differences among laboratories. These data can also serve as independent and external QA comparisons to data from the analytical duplicate QC samples. Additional checks can be made using the field duplicates and preparation duplicates.

Description of Quality Control Samples

Seven types of QC samples were used in the Northeastern survey:

- calibration blanks,
- reagent blanks,
- QC check samples (QCCS),
- detection limit QC check samples (DL-QCCS),
- matrix spikes,
- analytical duplicates,
- ion chromatography (IC) standards.

The QC samples are described below. Control limits were established for measurements of each of the QC samples. The results from each laboratory were examined with reference to these established limits.

One calibration blank per batch was analyzed immediately following the initial instrument calibration in order to detect instrumental drift or to test for evidence of sample contamination. The calibration blank was defined as a "0" concentration standard and contained only the matrix of the calibration standards.

For methods that required sample preparation, e.g., soil extractions, a liquid reagent blank was included in each batch of samples. The reagent blank, sometimes referred to as a process blank, was composed of only the reagents in their proportions used in preparing (extraction, digestion, etc.) a soil sample for analysis. This blank underwent the same procedures as a routine soil sample and was used to identify contamination of the reagents. If the observed concentration of the calibration blank or the reagent blank was greater than the CRDL, the instrument was rezeroed, the calibration was checked, and the source of contamination or error was investigated and eliminated. If the blank constituted 20 percent of the sample concentration and affected 25 percent of the routine samples, there was cause for reanalysis of the affected parameter.

A QCCS containing the analyte of interest at a concentration in the mid-calibration range was analyzed immediately following the standardization of an instrument, after the routine analysis of groups of ten samples, and after the last sample in each batch. The liquid QCCS was prepared from a source which was independent of the calibration standards and was used to determine the accuracy and consistency of instrument calibration. The control limit for the QCCS was 90 to 110 percent of the theoretical value (95 to 105 percent for sulfate parameters and 99 to 101 percent for particle size parameters). When an unacceptable QCCS value was obtained, the instrument was recalibrated and all samples analyzed beyond the last acceptable QCCS were reanalyzed. The QCCS were plotted on the QC chart and the 95- and 99-percent confidence intervals were calculated. The 99-percent confidence interval, the control limit, was required to be within the maximum control limit specified by the QA staff.

The DL-QCCS contained the analyte of interest at a concentration two to three times above the CRDL (Cappo et al., 1987). The purposes of this sample were to eliminate the necessity of formally determining the detection limit on a daily basis and to determine accuracy at the lower end of the linear dynamic range of measurement. The measured value of the DL-QCCS was required to be within 20 percent of the theoretical concentration. If the difference was greater than this limit, the source of error was identified and corrected, and acceptable results were obtained before initiating routine sample analysis. The CRDL often was far below the concentration of the lowest level analyte, hence, discriminating the DL-QCCS from background or instrument noise was difficult.

One matrix spike, i.e., a known quantity of analyte added to a sample aliquot, was examined in each batch to determine the sample matrix effect on the analytical laboratory measurements for most of the parameters. The spike concentration was approximately equal to the larger of the endogenous level or ten times the detection limit of the analyte being measured. The volume or weight of the added spike was required to be negligible for the purposes of calculation. Analytes that were extracted prior to analysis were spiked after extraction. If there was insufficient sample volume to spike all of the aliquots from one sample, the matrix spike analysis was performed on a per-aliquot basis.

If the spike recovery was not within 15 percent of the initial spike volume or weight, two additional samples were spiked with each of the analytes in question. The two additional samples were then analyzed and their respective recoveries were calculated. If the spike recovery in one or both of the additional samples was not within 15 percent, the entire batch of samples was reanalyzed for each of the parameters in question. The samples were diluted or the spike level was adjusted if the concentration of the matrix spike was not within the linear dynamic range for the analytical method.

One soil sample per batch was subsampled and analyzed in duplicate by the analytical laboratories. This QC sample, the analytical duplicate, was used in estimating the within-batch precision for each analytical laboratory and for identifying significant instrumental drift. The percent relative standard deviation (RSD) of each analytical duplicate pair, i.e., the duplicate and its companion routine sample, was calculated by dividing the standard deviation of the pair by the mean of the pair and multiplying this value by 100. If the percent RSD and the mean concentration of an analytical duplicate pair were greater than 10 percent and ten times the CRDL, respectively, then an explanation for the discrepancy was sought and another duplicate sample was analyzed. Sample analyses were stopped until instrumental control was restored, unless permission to proceed was obtained from the QA manager.

An ion chromatography (IC) resolution test was performed once per analytical run by analyzing an ion chromatography standard that contained approximately 1 mg SO4/L. If the resolution did not exceed 60 percent of the concentration, the column was replaced and the resolution test was repeated (Cappo et al. 1987).

Data Verification

Overview of Data Bases

The field sampling data and the analytical data were entered into the Northeastern data base using a compiled *dBase III* entry system at Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. These data also were sent to the QA staff at EMSL-LV for concurrent data verification. All data were double-entered into data sets and the two files were compared by computer for most of the data. Visual checking was a secondary approach and was used to check all units, thereby allowing errors in transcription to be identified and removed. The data bases progressed through three stages:

- raw data base,
- verified data base,
- validated data base.

The raw data base contains the data that were entered directly from the field data forms and analytical data packages through double entry by ORNL and EMSL-LV. The two entries were compared using a standardized computer comparison test and discrepancies were corrected so that the data sets were identical. One version was discarded and the other was frozen to become the official raw data base. A magnetic tape of this data base was sent to the National Computer Center (NCC) in Research Triangle Park, North Carolina, where the data tape was uploaded and made accessible to the QA staff.

Verification of the raw data base was accomplished by a systematic evaluation of completeness, precision, consistency, and coding accuracy. Discrepancies were flagged unless they could be corrected. After verification was completed, the data base was frozen and became the verified data base. A magnetic tape was generated and was sent to ORNL.

The verified data base underwent additional evaluation through a process called validation which resulted in a validated data base. The validation procedures included a specific assessment of outlying data points for inclusion or omission in data sets based on assigned levels of confidence. These data warrant special attention or caution by the data user during analysis of the survey results. After the data were evaluated and the suspect values were confirmed or flagged, the data were frozen as the validated data base (Turner et al., 1989).

Verification of Field Data

After locating specified sampling sites in designated watersheds, the sampling crews excavated, characterized, and sampled soil pedons representing the desired sampling classes (Blume et al., 1987). The pedons were characterized and sampled by United States Department of Agriculture (USDA) Soil Conservation Service (SCS) soil scientists who consistently utilized SCS computer-coded field data forms (SCS-SOI-232) to record the soil and general site descriptions. Use of the field data forms allowed sampling crews to gather comparable data for each pedon.

The completed field data forms were sent to ORNL where the data were entered into two data base subsets. The 232BA subset includes data from the first page of the field data form concerning general site and pedon characteristics. The 232HO subset includes data from the second, third, and fourth pages of the field data form concerning specific characteristics of the individual soil horizons. As ORNL staff were double-entering the raw data, QA staff at EMSL-LV were reviewing the data for outliers. During verification, a computerized system to verify field parameters for coding accuracy and completeness was not available; therefore, the data were reviewed manually.

Raw data were evaluated for each field crew. Outliers were identified and placed on discrepancy forms (see Appendix B) which were sent to the appropriate SCS state office for confirmation. The individual sampling crews reviewed these forms and entered either the corrected values or a notation indicating that the requested information could not be discerned. In either case, all outliers identified on the form were addressed and initialed by the reviewer. The discrepancy forms were returned to the QA staff who edited the corrections on the original field data forms. In all, three separate sets of discrepancy forms were sent to the sampling crews during data verification. Various outliers were overlooked during the initial review, because of the hand-checking procedure, but surfaced during the second and third reviews.

When the raw data base became accessible to QA personnel, a set of procedures for entering and editing the data base was employed. Editing was accomplished on a working copy of the official raw data base supplied by ORNL. All changes were made on this data base through a special editing program, thereby protecting the official raw data base.

A subset of the raw data base was keyed into the analysis program. The subset, sorted by state, was moved into a temporary working file and underwent manual editing. After completion of editing, the manual system was exited and a transaction file of both edited and original data was created automatically. At the end of each editing session, the transaction file was printed and reviewed.

After the edits were verified, the local master data base was updated with the edited information in the transaction file. This information was also transferred into a history file, which recorded all transactions made on the local master data base. The verified master data base was completed in August 1986.

ORNL personnel ran a thorough check by comparing data on the tape with the original field data forms. Occasional entry and editing errors were discovered and, after correction, a second tape was generated in September 1987. It was decided that QA staff would make no further edits on the official verified data base. Subsequent discoveries of outliers were jointly discussed and documented by EMSL-LV and ORNL. Further changes in the data base were made only upon written confirmation of the QA staff.

Additional tests were performed on the verified data which generated a small set of outliers. Discrepancy forms identifying these outliers were sent to the appropriate SCS state offices for confirmation. A new list of edits was compiled by QA staff and was sent to ORNL for entry. EMSL-LV also entered the edits into a working file that was maintained by the QA staff. Comparisons of the ORNL and EMSL-LV files were made to evaluate the completeness and consistency of edits.

Verification of Analytical Data

Analytical data reported on 100-level data reporting forms and 200-level blank-corrected data forms were entered into a data set by ORNL. A magnetic tape of the data was added to the catalogue file at NCC, where it was loaded for remote access by the QA staff. Exceptions programs, used to highlight discrepancies in the data sets, were applied during data quality assessment.

The steps identified below were established to identify and correct suspected data errors. Information obtained by this process was used to edit data on the magnetic tapes sent by ORNL. New data and flags were entered into the raw data set to correct or flag the original data.

Review of Data Packages

When data packages were received from the analytical laboratories, the QA staff checked to ensure that the correct sequence and number of forms were submitted and that each form contained data for all samples in the batch. The laboratory manager's signature and the date of analysis was confirmed on each form. Each data package was then subjected to the following QA/QC checks:

- Audit data were evaluated with the data verification template (see Appendix B).
- The RSDs of all duplicate pairs were checked.
- Standard analyte relationships were evaluated.
- Blank concentrations were checked for compliance, i.e., less than the CRDL as outlined previously in Table 2-2.
- Instrument detection limits (IDLs) were checked for compliance, i.e., less than their corresponding CRDLs.
- Matrix spikes were checked for compliance in preparation, i.e., concentrations were ten times the CRDL or twice the endogenous level, whichever was greater; data were checked to

ensure that spike recoveries were within 15 percent of the original spike concentration.

- QCCS data were checked for compliance, i.e., that the values were within the calculated control limits.

- Reported and blank-corrected data were checked for proper calculations.

The QA staff compiled verification reports for each batch data package submitted. A response letter describing potential discrepancies within the reported data and occasionally suggesting where errors may have occurred, (e.g., transposed numbers or erroneous dilution factors), was sent to each laboratory after evaluation of the data package. Through the use of Form 500 (see Appendix B), the laboratories were required to respond promptly with confirmation or reanalysis of the parameters in question. Reanalysis was performed on whole batches of samples rather than on individual samples.

Compliance for Quality Control Check Samples

Analysis of a QCCS was not required for the titrimetric analytical methods used to determine the cation exchange capacity (CEC) and exchangeable acidity parameters. For the other analyses, the QCCS concentrations were formulated to represent an approximate mid-range of the routine samples. The QCCS data were used to check calibrations.

The chemical characteristics and concentrations of the QCCS were known to the analytical laboratories, hence, it was expected that the observed values of the QCCS would be within 10 percent of their respective theoretical values.

Due to the importance of the sulfate analysis to DDRP, the observed values were required to be within 5 percent of the theoretical values. The QCCS observations outside of these ranges are tabulated in Table B-1 of Appendix B. The application of a Type I error equation (Aronoff, 1984) generated a list of QCCS values whose compliance was estimated at the 0.05 significance level.

The large number of QCCS samples outside of the range for the particle size classes suggest that the control limits were too tight for this parameter group. Other low concentration parameters were also susceptible to falling outside of the range.

Compliance for Quality Assurance Samples

The audit pairs and the field, preparation, and analytical duplicates were used in the preliminary QA/QC assessment. The QA acceptance criteria, i.e., audit windows, initially were calculated for each of the parameters as the 95-percent confidence interval of audit sample data from the DDRP Northeastern Soil Survey. The audit sample windows were updated periodically on the basis of incoming data from the analytical laboratories. Audit pairs were first checked for their inclusion within the audit windows. The precision of each pair was estimated by calculating the percent RSD, with more than 10 percent RSD being acceptable if the mean of the pair was less than 10 times the CRDL.

Standard Relationships

The following relationships were tested against all routine samples to check for random or systematic errors. These checks were critical because they provided verification checks independent of QA samples.

- Particle Size Analysis:
  SAND + SILT + CLAY = 100
  The summation of total sand, silt, and clay in mineral soil samples should equal 100 percent ±0.1 percent. Also, samples labeled as organic soils are checked for having 12 percent or more organic carbon.

- pH: PH_H2O > PH_002M > PH_01M

  Calcium ions in the calcium chloride extract displace hydrogen ions by mass action on the exchange sites, thereby increasing the hydrogen concentration in the soil solution relative to that of the water extract. A higher concentration of calcium will more effectively displace hydrogen ions and will result in a lower pH.

- Cation Exchange Capacity (CEC):
  CEC_OAC > CEC_CL

  Ammonium ions in a buffered (pH 7.0) ammonium acetate solution displace other cations from exchange sites. This method was used in conjunction with AC_BACL to establish the total CEC in the soil. Ammonium in an unbuffered ammonium chloride solution provides a more accurate estimation of the actual CEC of the soil when included with AC_KCL. The CEC in ammonium acetate is theoretically greater than the CEC in ammonium chloride.

- Exchangeable Acidity:
  AC_BACL > AC_KCL

  A buffered (pH 8.2) barium chloride triethanolamine solution was used to assess the total potential acidity. The unbuffered potassium chloride method estimates the actual exchangeable acidity in soils. Generally, the exchangeable acidity in potassium chloride is less than that in barium chloride triethanolamine (exceptions include some coarse-textured or low CEC soils).

- Extractable Sulfate:
  SO4_PO4 > SO4_H2O

  The phosphate anion, because of its size and chemical properties, readily exchanges with the sulfate anion. The phosphate extraction gives an indication of the total exchangeable sulfate in the soil. The water extraction measures only those sulfate ions that are easily displaced and is an accepted indicator of available sulfate in the soil. Generally, the sulfate concentration in the water extraction is less than that found in the phosphate extraction (exceptions include some soils with low sulfate adsorption or high organic matter).

- Sulfate Isotherms:
  SO4_0 < 2 < 4 < 8 < 16 < 32

  The isotherm relationship is a response to increased concentrations of sulfate. The isotherms should increase monotonically with the amount of sulfate in the initial solution.

Internal Consistency

Most of the verification checks and evaluations of analytical laboratory measurements were performed on data from QA and QC samples. Although an assessment of data quality could be drawn from these samples, the QA staff decided that an additional evaluation was needed to identify specific errors in the data for the routine (non-QA) soil samples. The purpose of this evaluation was to identify values for each analytical parameter that were not consistent with the majority of values observed. These values were checked for errors in transcription, data entry, or editing. If no discrepancies were encountered, these data values were qualified, or "flagged", as routine data outliers with an "X" flag (see Appendix A). Time did not permit the QA staff to identify the cause of all outliers, nor was it feasible to confirm the accuracy of outliers with the laboratory personnel.

An internal consistency program created at ERL-C was used to identify the routine data outliers The first step was to correlate analytical data for each parameter with all other analytical parameters measured in the Northeastern survey. The strongest correlations, based on the coefficient of determination (r^2), were investigated. When the r^2 value generated by the correlation of one parameter with another was greater than 0.80, the correlation having the highest r^2 was selected and the internal consistency computer program was applied to all of the routine data points. If r^2 for the highest correlations was less than 0.80, a separation of data between organic and mineral samples was used in order to ascertain whether the groupings had an effect on the correlation. The correlation was used if r^2 increased significantly after the organic and mineral samples were correlated separately.

In some cases, the values for one parameter did not correlate well with values for any other parameter. In these cases, a percentage of the highest and the lowest values for that parameter were checked for errors. Correlations were not performed on parameters within the same extract or from the same measurement, e.g., CA_OAC values were not correlated with MG_OAC values even though the resulting r^2 value had the highest value. The reason for this decision is that it was recognized that certain errors, e.g., incomplete extraction, would not be identified by performing correlations within the same extracting solution. Although correlations were performed for particle size parameters, the highest and lowest values in each particle size class were also checked.

The internal consistency program was designed using a weighted linear regression model (SAS, 1986) because the data exhibited heteroscedasticity, i.e., the variances were not the same for the entire population. The weighting factor (w) which was used in the regression was calculated as the reciprocal of the analyte concentration of the independent variable (w = 1 / x). Some parameters, e.g., pH, did not have to be weighted. The correlation was established by plotting values for one parameter on the X-axis and values for another parameter on the Y-axis. Outliers were defined as those points having a studentized residual (Belsley et al., 1980) of 3.0 or greater. The X and Y-axes of each parameter then were reversed and the regression was repeated. The results from both regressions were combined in order to identify the outliers.

For each regression, the studentized residual (SR) was calculated by subtracting the regression estimate of the dependent variable from its corresponding observed value and dividing by the estimated standard error of the residual, as follows:

$$SR = (y_i - \hat{y}_i) \div [S_{(i)} \cdot (1 - h_i)^{1/2}]$$

where: y_i is the ith value of the dependent variable

$\hat{y}_i$ is the ith predicted value of the dependent variable by the regression equation

$S_{(i)}$ is the standard error estimated with the ith observation excluded

h_i is the ith leverage factor

The studentized residual is an appropriately robust technique used to investigate outlying data points. A possible limitation in the capability of the studentized residual to determine an outlier was that the outlier itself strongly influenced the regression estimates of the slope or intercept, thereby abnormally affecting the value of the residual.

Another outlier measurement technique involved the use of a DFFITS statistic (Belsley et al., 1980). DFFITS is a measure of the change in the predicted value resulting from the exclusion of a specific observation in the regression analysis. The DFFITS statistic was used to examine the significance of large differences in residuals and was calculated as follows:

$$DFFITS = (\hat{y}_i - \hat{y}_{(i)}) \div (S_{(i)} \cdot h_{(i)}^{1/2})$$

where: $\hat{y}_i$ is the ith predicted value with the current observation included

$\hat{y}_{(i)}$ is the ith predicted value with the current observation excluded

$S_{(i)}$ is the standard error estimated with the ith observation excluded

$h_{(i)}$ is the leverage factor with the ith observation excluded

As in the studentized residual, division by the estimated error normalized the statistic to allow comparision among points of varying precision. As a result, controlling data points that might unduly affect the predicted value of the dependent variable tended to have a high DFFITS value. The critical point which was used to define a high value, i.e., the critical DFFITS, and its corresponding outlier was calculated as follows:

$$2\,[(m + 1) + n]^{1/2}$$

where: m is the number of independent variables

n is the number of points or observations regressed

A data outlier was identified as any data point exceeding the critical values which had been defined for the studentized residual or DFFITS statistic. These points were temporarily removed from the set of observations being analyzed. Using the remaining data, a second regression was performed on the same parameters. Utilizing the regression equation, i.e., slope and intercept estimates, from the second regression performed and the mean and corrected sum of squares from data points defined as outliers in the first regression, a residual test was performed to examine and return data outliers to the set of "good" or viable data points. Any outliers that failed to pass this test were considered outliers and underwent additional internal consistency checks. Results were checked for accuracy in transcription against the values in the data package and, where necessary, corrections were made.

After edits were made in the data base, the internal consistency program was repeated and a second set of outliers was generated. Any new outliers which appeared in the second correlation were checked for accuracy. No errors in transcription were found in the second regression.

Table B-2 in Appendix B contains a list of correlations that were performed for each parameter, the parameter groups, and the r^2 values for the first and second correlations. Most of the correlations resulted in r^2 values greater than 0.80. When correlations were performed for the sulfate isotherms and for total sulfur and nitrogen, it was observed that a disproportionate percentage of the outliers were organic samples having high variability. Separating the organic horizons from the mineral horizons aided in identifying mineral soil outliers.

The following types of errors in the data base for the Northeastern survey were identified by the internal consistency checks and were subsequently confirmed or corrected:

- data entry errors, i.e., values from the analytical laboratory data packages that were entered incorrectly

- transcription errors, i.e., data that were transposed or transcribed at the analytical laboratories incorrectly, e.g., 3.54 instead of pH 5.34; most of these suspect values had been identified earlier and confirmation requests were sent to the laboratories where the values were corrected, although the values had missed the editing loop

- batch errors, i.e., systematic or sporadic calculation errors that were discovered when most or all of the data in specific batches were outlying

- laboratory errors, i.e., systematic or sporadic calculation errors that were discovered when some or all of the data in batches from a specific laboratory were outlying

Data Quality Objectives

To address the DDRP objectives, conclusions must be based on scientifically sound interpretations of the data base. To achieve this end, the EPA requires all monitoring and measurement programs to have established objectives for data quality based on the proposed end uses of the data (Stanley and Verner, 1985; Blacker et al., 1986 [Internal Document]). Computer models are being used to predict results and to test hypotheses. The utility of the data, and thus the project itself, is defined by the ability to confirm, reject, or discriminate among hypotheses. The primary purpose of the QA program is to increase the likelihood that the resulting data base meets or exceeds specific DQOs. Through the proper development of DQOs, the quality of data can be quantified, thereby allowing the data user to evaluate various hypotheses. In practice, DQOs are statements of the levels of uncertainty that a data user is willing to accept in the results derived from the data.

The DQOs for the Northeastern survey (Coffee et al., 1987) were established for detectability, precision, representativeness, completeness, and comparability (U.S. EPA, 1985ᵃ). Due to the naturally low analyte concentrations in the soils under investigation, contract-required detectability standards were established to further enhance interpretability of the data base. The DQOs for precision are quantitative criteria that were developed for the analytical component of the data collection activities and the measurement system used in the Northeastern survey. Precision DQOs were established for the mineral soils but not for the organic soils. The DQOs for representativeness, completeness, and comparability were somewhat qualitative in nature and were assessed primarily by the research design and selection of methodologies. There were no DQOs established for accuracy, although an attempt has been made in this report to relate accuracy to interlaboratory differences.

Detectability

An important factor to consider in the evaluation of data quality is the detection limit, which is the lowest concentration of an analyte that an analytical process can reliably detect. The primary consideration is whether a measured sample value can be considered significantly different from the measured value of a sample blank. The probability that an analytical signal is not simply a random fluctuation of the blank is dependent on how many standard deviations the analytical signal varies from the mean value of blank responses (Long and Winefordner, 1983). The specific application of detectability in the Northeastern survey required the investigation of precision in low concentration samples.

A commonly recognized value for the detection limit is three times the standard deviation of the blank samples (American Chemical Society, 1983). A signal measured at this level or greater would have less than a 0.1 percent chance of being the result of a random fluctuation of the blank, assuming the blank samples have a normal distribution. In the absence of blank samples, low concentration replicate samples are often used to estimate the standard deviation expected of blank samples. Although liquid blank samples have been used extensively in the aquatics surveys of the National Surface Water Survey, development of a soil blank suitable for system-wide use in the DDRP has not been feasible. With this in mind, the following three types of detection limits are described in this report.

(1) All analytical laboratories were required to satisfy the contract-required detection limit (CRDL) for specified parameters, as presented in Table 2-8. The CRDLs were established for instrument readings in the analytical phase only.

(2) A calculated instrument detection limit (IDL) was used to estimate the lowest concentration of an analyte that the analytical instruments used by the laboratories could reliably detect. Although IDLs were calculated from analytical blank samples and were reported by the laboratories, these values are not included in this report. Instead, an independent check of the IDLs was possible by examining the variability in the DL-QCCS samples and by assuming that the variability of this low level sample should have been about the same as that of the blank samples. The IDLs reflect variability in the analytical phase only.

(3) It is recognized that laboratory analysis is only one of many steps in the overall process of generating raw data for a soil sample collected from the field. If it were possible to route "soil blank" samples with zero concentration of analyte through the sampling crews and subsequently through all phases of the measurement system, a system detection limit (SDL) could be estimated. Overall variability in the blank sample would encompass variability in sampling, preparation, extraction, and analysis, and would include sample contamination at any of these phases. Calculation of a SDL from such a sample would allow a data user to identify when any given soil sample had a measured concentration that could be considered as statistically different from that of a reagent blank or calibration blank. For this report, reasonable substitutes for blank samples are the field duplicates which are routed through the major components of the measurement system and exhibit many of the features that would be expected in soil blanks. By selecting the field duplicates of least concentration, e.g., the 10 percent of duplicate samples with the lowest average concentration, the resulting variability would be expected to parallel that of system-wide blanks.

The calculated IDL was estimated as three times the pooled standard deviation of a low level DL-QCCS. The SDL was estimated as three times the pooled standard deviations of the lowest ten percent of all field duplicate pairs. These limits, together with the CRDL and the converted IDL (the calculated IDL in comparable reporting units), are given in the Results and Discussion, Section 3. The effect of adjusting CRDLs for certain parameters during the course of the survey is also examined.

An important factor to consider in the evaluation of detectability is the implication of the calculated detection limits for data quality of the routine data set. By estimating the percentage of data from the routine samples

Table 2-8. Data Quality Objectives for Detectability and Analytical Within-Batch Precision

Parameter	Reporting units	CRDL[a]		Precision DQO[b]		
		units	mg/L	Lower tier SD	Upper tier RSD	Knot units
MOIST	wt %	ne	ne	ne	ne	ne
SP_SUR	m^2/g	ne	ne	ne	ne	ne
SAND[c]	wt %	na	na	1.0[d]	—	—
SILT[c]	"	na	na	1.0	—	—
CLAY	"	na	na	1.0	—	—
PH_H2O	pH units	na	na	0.15[d]	—	—
PH_002M	"	na	na	0.15[d]	—	—
PH_01M	"	na	na	0.15[d]	—	—
CA_CL	meq/100g	0.003	0.05	0.03	15%	0.20
MG_CL	"	0.011	0.05	0.03	15%	0.20
K_CL	"	0.003	0.05	0.03	15%	0.20
NA_CL	"	0.006	0.05	0.03	15%	0.20
CA_OAC	meq/100g	0.006	0.05	0.03	15%	0.20
MG_OAC	"	0.011	0.05	0.03	15%	0.20
K_OAC	"	0.006	0.05	0.03	15%	0.20
NA_OAC	"	0.006	0.05	0.03	15%	0.20
CEC_CL	meq/100g	0.002	0.01[e,f]	0.25	10%	2.5
CEC_OAC	"	0.002	0.01[e,f]	0.25	10%	2.5
AC_KCL	"	0.75	0.25[f]	0.50	20%	2.5
AC_BACL	"	0.11	0.40[f]	0.50	20%	2.5
AL_KCL	"	0.80	0.10	0.50	20%	2.5
CA_CL2	meq/100g	—	—[g]	—	5%[d]	—
MG_CL2	"	0.0007	0.05	—	10%[d]	—
K_CL2	"	0.0002	0.05	—	10%[d]	—
NA_CL2	"	0.0004	0.05	—	10%[d]	—
FE_CL2	"	0.0005	0.05	—	10%[d]	—
AL_CL2	"	0.0001	0.05	—	10%[d]	—
FE_PYP	wt %	0.005	0.50	0.05	15%	0.33
AL_PYP	"	0.005	0.50	0.05	15%	0.33
FE_AO	"	0.005	0.50	0.05	15%	0.33
AL_AO	"	0.005	0.50	0.05	15%	0.33
FE_CD	"	0.002	0.50	0.05	15%	0.33
AL_CD	"	0.002	0.50	0.05	15%	0.33
SO4_H2O	mg S/kg	2.0	0.10	1.0	10%	10.0
SO4_PO4	"	2.0	0.10	1.0	10%	10.0
SO4_0	mg S/L	0.10	0.10	0.05	5%	1.0
SO4_2	"	0.10	0.10	0.05	5%	1.0
SO4_4	"	0.10	0.10	0.05	5%	1.0
SO4_8	"	0.10	0.10	0.05	5%	1.0
SO4_16	"	0.10	0.10	0.05	5%	1.0
SO4_32	"	0.10	0.10	0.05	5%	1.0
C_TOT	wt %	0.01	0.010[h]	0.05	15%	0.33
N_TOT	"	0.01	0.010[h]	0.01	10%	0.10
S_TOT	"	0.01	0.010[h]	0.01	10%	0.10

[a] Contract-required detection limit is expressed in reporting units and mg/L, respectively.
[b] Precision DQOs below and above the knot separating the lower tier (standard deviation in reporting units) and the upper tier (relative standard deviation in percent); the knot is given in reporting units.
[c] Precision DQOs were not established for size fractions of this parameter.
[d] One precision DQO was established over the lower and upper tier range for this parameter; no knot was required.
[e] Unit is meq/L for this parameter for flow injection analysis.
[f] Unit is meq for this parameter for titration.
[g] CRDL was reported as standard deviation of ten nonconsecutive blanks.
[h] CRDL unit is wt % for this parameter.
NOTE: na CRDL is not appropriate for this parameter.
ne CRDL and precision DQOs were not established for MOIST and SP_SUR.

that were greater than the corresponding SDLs, specific parameters were identified that might not have been measured with sufficient precision to satisfy the requirements of data users. This was not necessarily the result of improper CRDLs, for it is evident that the instrumental error was the source of only a small portion of the variability in the low concentration field duplicates used to estimate the SDLs.

Precision

Development of the Precision Objectives

The precision DQOs for the Northeastern survey were established for analytical within-batch precision for the mineral soils for the parameter listed in Table 1-1 of Section 1. Of the 12 physical parameters, precision DQOs were established for only the sand, silt and clay. Precision DQOs were established for all 39 chemical parameters listed. There were no specific DQOs established for the sampling or preparation phases of the survey. The initial DQOs were based on the requirements of EPA data users, the selection of appropriate methods to obtain the required data, and the results of a pilot study. Modifications were implemented based on review comments from the users and cooperating scientists. In addition, the analytical results from specific methods, procedures, and instrumentation were useful in the adjustment of DQOs for future DDRP surveys.

The primary characteristics of the precision objectives were the development and implementation of a two-tiered system for characterizing the DQOs. Similar parameters were grouped together according to their type of reporting units. Intralaboratory within-batch precision goals were defined, based on a percent RSD for concentrations above a specific level, defined as the "knot", and an absolute standard deviation for concentrations below the knot (see Table 2-7). The upper tier concentration range above the knot defines the region of the data where the acceptable uncertainty limits for duplicate analyses are expressed as a percentage of the observed mean. The lower tier concentration range below the knot defines the region of the data where the analytical results are absolute and expressed as a standard deviation in reporting units. This system avoids setting restrictive precision requirements for low concentration samples which generally are more difficult to analyze with a high degree of precision. The knot was established by dividing the precision objective at the lower tier by the precision objective at the upper tier, times 100 (see Figure 2-2).

The CRDLs and precision DQOs were not established for MOIST and SUR. It was also not appropriate to establish CRDLs for the particle size or pH parameter due to the nature of their measurement procedure, i.e., by weighing and potentiometric readout, respectively.

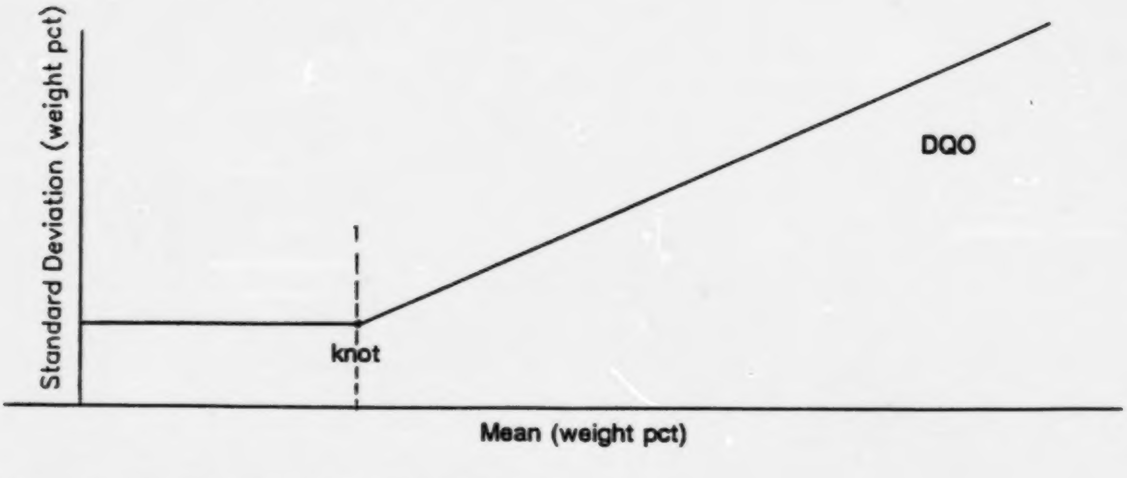


Figure 2-2. Example of a two-tiered precision objective.

Two-tiered DQOs (and knot values) were not established for sand, silt, and clay in the physical parameter group, six for the three pH determinations, or for the cations in 0.002M calcium chloride. Instead, one DQO was established either as a standard deviation or a %RSD for the total concentration range for these three parameter (see Table 2-8).

Data from the homogenized natural audit samples were used to assess the DQOs for analytical within-batch precision because they had no sampling error and were assumed to have negligible preparation error. As such, the precision DQOs developed for the Northeastern survey were not intended to serve as project level DQOs.

Estimation of the Data Collection Error

For any large survey, the collection of data is a multi-phase process. In the DDRP, those phases are field sampling, sample preparation, and sample analysis. The QA samples were introduced at these different data collection phases so that analytical data from the samples could be used to control and assess the uncertainty for each phase. For example, data from field duplicates can be used to estimate the confounded error associated with field sampling, sample preparation, and sample analysis. Data from the preparation duplicate samples can be used to estimate the confounded error associated with subsampling in the preparation laboratory sample and analysis at the analytical laboratory. Data from the audit samples can be used to estimate the error associated with sample analysis. The audit samples are assumed to have negligible preparation error for the purposes of the error estimates that are based on the following model:

$$y = \mu + \epsilon$$

where: y is an observed sample characteristic

μ is the true sample characteristic

ϵ is the data collection error, which is assumed to be the sum of the errors generated by the three independent data collection phases

Standard operating procedures, or protocols, were followed in each phase of the Northeastern survey. Depending on its limitations or assumptions, each operating procedure induces a random error for each physical or chemical characteristic of a soil sample. The sum of the errors induced by each procedure can be defined as data collection error, which is treated as a random variable. It is necessary to characterize this variable in order to identify the effect of the error on the routine soil samples. This involves identifying the distributional form and estimating the moments.

The identification of the error distribution requires a large number of replicate measurements which, from a budgetary and logistical standpoint, imposes a serious limitation. However, a relatively small number of observations can be used to estimate the first two moments, i.e., the mean and variance, of the data collection error. The mean and variance are sufficient to measure the precision and accuracy of the routine data in an additive model, where the observed analyte concentration is assumed to be the sum of the true analyte concentration and the data collection error. For this report, the standard deviation in reporting units and the RSD, i.e., coefficient of variation, in percent, are used to measure precision.

The within-batch precision component measures the reproducibility of audit sample data for a given set of soil samples analyzed for one analytical run by one laboratory. The between-batch precision component measures the reproducibility of audit sample data for different batches of soil samples analyzed on different days or at different times in any one day by the same or different laboratories. It is expected that the within-batch variability is smaller than the between-batch variability.

One pair of natural audit samples was placed in each of the 55 batches for a total of 55 audit sample pairs for the Northeastern survey. To assess the within-batch precision, the standard deviations for the natural audit pairs were pooled by averaging the variances and taking the square root to generate a within-batch standard deviation. For between-batch precision a standard deviation was calculated for the pooled means of the audit pairs.

It was found that the variance changes with analyte concentration, and it was not possible to identify a normal relationship between the soil analyte concentration and the error variance. However, the range of the soil analyte concentration was arbitrarily divided into intervals, i.e., windows, by grouping clusters of data in such a way that the error variance was relatively constant within each window. It was then possible to fit a step function across the windows to represent the error variance for the entire concentration range.

For each QA sample type, a step function was used to represent the appropriate standard deviation. Values for the fitted step function were pooled and used as an estimate of the associated standard deviation, e.g., data from the preparation duplicates were used to estimate the standard deviation of the confounded preparation and analytical error.

The standard deviations were pooled (s_p) by using the degrees of freedom (df) as a weighting device according to the formula:

$$s_p = [\ \Sigma_{\{i=1,k\}} (df_i \cdot s_i) \div \Sigma_{\{i=1,k\}} df_i\ ]^{1/2}$$

where: s_p is the pooled standard deviation within each window.

s_i is the standard deviation for the ith window with corresponding degrees of freedom df_i.

The RSD was used to assess data in the upper concentration ranges and was obtained by dividing the pooled standard deviation by the weighted mean.

It was also important to evaluate the effect of measurement precision on the routine sample data. Since the error standard deviation changed with analyte concentration, the expected standard deviation was estimated by considering its variability over the concentration range of routine samples. In order to estimate this effect, the standard deviations for different windows pooled with weighted proportions of routine samples grouped by sampling class/horizon criteria within the respective windows. This pooled value, delta (δ), is used as a measure of system-wide data uncertainty in the routine sample data due to data collection error. The use of delta here is as a figure of merit rather than as a standard deviation per se. Delta is defined as:

$$\delta = \Sigma_{\{i=1,k\}} (P_i \cdot s_i) \div \Sigma_{\{i=1,k\}} P_i$$

where: δ is the pooled standard deviation for all windows over the concentration range

P_i is the proportion of routine samples in the ith window

s_i is the estimated standard deviation for the ith window

Occasionally, a lack of QA sample data within the concentration limits of a particular window made it impossible to calculate a standard deviation for that portion of the data set. In those cases, delta is the conditional measure of data uncertainty, the condition being dependent on the availability of QA data. Hence, certain windows are excluded from the calculation of delta.

An assumption is stated that the sampling class/horizon groups define homogeneous sets of soil samples, each having a specific variance. The 38 sampling classes and the 24 primary horizon types associated with these classes are known "effects" that define soil differences in the Northeastern survey. By specifying these characteristics in the model, the variation due to these effects was removed. Table 2-9 presents the number and percentage of primary horizon types selected as a basis for the sampling class/horizon criteria used in grouping the 1,634 routine samples, and the number of sampling classes seperated in each horizon.

Accuracy (Interlaboratory Differences)

Accuracy is the ability of a specific component of a measurement system to approximate a true value. The audit samples used in the Northeastern survey were natural soil samples. Their "true" chemical composition and physical characteristics are thus unknown. Natural soil samples were used as audit samples because a procedure for preparing synthetic soil samples has not been established. Therefore, accuracy of the analytical data cannot be determined because neither synthetic soil audit samples nor natural soil

Table 2-9. Primary Horizon Types for Sampling Class/Horizon Groups

Horizon types	Routine samples n[a]	 %	Sampling classes represented[b]
A	91	5.6	32
AB	6	0.4	5
AE	3	0.2	3
Ag	2	0.1	2
Ap	36	2.2	17
BA	13	0.8	7
BC	91	5.6	26
BE	5	0.3	3
Bg	43	2.6	7
Bh	46	2.8	15
Bhs	51	3.1	17
Bs	168	10.3	19
Bw	252	15.4	28
Bx	43	2.6	2
C	254	15.6	30
CB	2	0.1	2
Cg	61	3.8	11
Cr	111	6.8	19
E	71	4.3	23
EB	3	0.2	3
Eg	4	0.2	4
Oa	169	10.3	32
Oe	99	6.1	29
Oi	9	0.6	3

[a] N = 1,634, but one type was unidentified.
[b] N = 339.

audit samples of known composition could be used as audit samples. An international interlaboratory comparison study, however, is currently being conducted to provide data on the chemical composition and physical characteristics of the natural audit samples (Fenstermaker et al., in preparation). Data from the analyses of the audit samples by 22 external laboratories can possibly be considered to represent the best available estimate of the true concentration of the various parameters in those samples. In this report, data from the natural soil audit samples are used to establish interlaboratory differences.

Absolute Differences

The absolute difference (d_i) is defined as the variation between the mean of a repeated measurement for a given laboratory and the mean for the measurement among all laboratories, as follows:

$$d_i = | x_i - X |$$

where: d_i is absolute difference for the ith laboratory

x_i is mean for the ith laboratory

X is mean for all laboratories

Significant Differences Among Laboratories

For each of the parameters, the analysis of variance (ANOVA) was used to determine the significant differences among the audit sample data reported by the analytical laboratories. An initial review of the data showed that the analytical variances across audit sample types were not identical. Because of this lack of homogeneity, a nested ANOVA model (Steel and Torrie, 1960) was used for each audit sample type to test the significance of laboratory differences by comparing laboratory means, based on a similar approach in Schmoyer et al. (1988). The model is as follows:

$$Y_{ijk} = \mu + L_i + p_{ij} + \epsilon_{ijk}$$

where: Y_{ijk} is the ith laboratory observation in the jth batch of the kth audit sample

μ is the expected value of the audit samples

L_i is the ith analytical laboratory effect

p_{ij} is the jth batch effect within the ith laboratory

ϵ_{ijk} is the random error

Where laboratory differences were significant, a pair-wise comparison was performed on the laboratory means by using Scheffe's multiple comparisons test (Arnold, 1981). The results of this test were used to select values of high significance and to describe the ranking order for the analytical laboratories.

Pooled Data for Laboratory Differences

Data pooled across audit samples to eliminate horizon effects were used to establish each laboratory's performance for individual parameters. This was accomplished by ranking the laboratories according to the magnitude of their difference from the grand mean (rank 1 to 4, smallest to largest difference) after first comparing the difference to the overall laboratory mean. Only two of the five audit sample types, the Bs and Bw audit samples, were analyzed by all four laboratories (see Table 2-7). Interlaboratory differences were determined, therefore, by pooling only the data for the Bs and Bw audit samples for each laboratory, as follows:

$$\frac{\Sigma_{(a = Bs,Bw)}\ (d_{ia} \cdot n_{ia}) \ + \ \Sigma_{(a = Bs,Bw)}\ n_{ia}}{\Sigma_{(a = Bs,Bw)}\ (X_a \cdot n_a) \ + \ \Sigma_{(a = Bs,Bw)}\ n_a} \cdot 100$$

where: d_{ia} is absolute difference for the ith laboratory and the ath audit sample

n_{ia} is number of samples for the ith laboratory and the ath audit sample

X_a is mean for all laboratories for the ath audit sample

n_a is total number of samples for the ath audit sample

Pooled Data for Audit Sample Differences

Data pooled across laboratories to eliminate analytical laboratory effects allowed an evaluation to be made of the mean laboratory differences for the five audit samples types. If the range of chemical and physical data of the audit samples is comparable to that of the routine samples in the survey, an evaluation can be made of the ability of the laboratories as a group to analyze certain soils using the specified analytical methods. For example, if the interlaboratory differences were very high for the organic audit sample for a parameter determined by a specific analytical method, the method itself could be in question regarding its ability to properly describe the determination of that parameter. The overall laboratory difference for each audit sample was determined as follows:

$$\frac{\Sigma\ (d_{ia} \cdot n_{ia}) \ + \ \Sigma\ n_{ia}}{X_a} \cdot 100$$

where: d_{ia} is difference for the ith laboratory and the ath audit sample

n_{ia} is number of samples for the ith laboratory and the ath audit sample

X_a is mean for all laboratories for the ath audit sample

Representativeness

The evaluation of representativeness includes: (1) determining whether the routine samples collected were representative of the sampling class characteristics, (2) assessing the homogenization procedure by measuring the ability of each preparation laboratory to prepare representative subsamples from the bulk soil samples collected by the sampling crews, and (3) assessing the ability of the QA samples to adequately represent the range and frequency distribution of analyte concentrations in the routine samples.

Data from the preparation duplicates were used in the second assessment, while the KolmogorovSmirnov two-sample test, i.e., the KS-statistic, was used to estimate the maximum distance between two data sets as a measure of resemblance between the sets (Conover, 1980).

Three data sets encompassing data for the routine samples (RS), the field duplicates (FD), and the preparation duplicates (PD) were used in the last assessment. The FD and PD sets were tested independently against the RS set by using the p05, p50, and p95 percentiles to assess the range and frequency distribution within the data sets. The significant KS-statistics, i.e., significant at the 0.05 level, were defined according to the critical value (V_c) for each data set comparison. The critical value is based on a sample size n_1 and n_2 for the data sets being compared, where:

$$V_c = 1.36\ [(n_1 + n_2) + (n_1 \cdot n_2)]^{1/2}$$

This algorithm yielded critical values for the data set pairings, where V_c for FD_RS is 0.089 and V_c for PD_RS is 0.186. If the KS-statistic exceeded the critical value for a particular data set pairing, the QA data set was not representative of the distribution of routine samples.

Completeness

Soil sampling protocols in the Northeastern survey specified the sampling of 100 percent of the designated pedons. The soil preparation protocols specified that each batch of samples sent to an analytical laboratory included a preparation duplicate sample. The soil analysis protocols specified the analysis of all samples collected for 90 percent or more of the parameters. These three aspects of completeness were evaluated using the Northeastern verified and validated data bases.

Comparability

Data comparability is ensured by the uniform use of documented procedures for soil collection, preparation, and analysis and by the use of equivalent units for reporting the data. The analytical methods and associated QA/QC protocols that were used in the Northeastern survey were selected so that the data could be compared with other similar data bases, e.g., the DDRP Southern Blue Ridge Province data base. On-site system audits and thorough evaluations of analytical data were employed to ensure that the procedures were being followed correctly.

The DDRP Analytical Methods Manual (Cappo et al., 1987) contains detailed descriptions of each of the analytical techniques, including examples of calculations and appropriate references. The internal QC procedures for each method are described in an introductory section and are summarized in tabular form. The QC protocols also are described within each of the analytical method descriptions. Data quality objectives, data qualifiers, and decimal reporting requirements are listed in tabular form.

The DDRP Quality Assurance Plan (Bartz et al., 1987) was based on previously developed planning documents for the National Surface Water Survey. The QA Plan includes several introductory sections describing the project organization, sampling strategy, and field operations. The QA objectives and the sampling, preparation, and analytical QC procedures are described in detail and are also summarized in tabular form. Analytical methods are listed with the appropriate references. These methods generally are descriptive of the methods specified in the overall SOW as well as the subsequent EPA special analytical services solicitations.

Before it can be ascertained whether the field sampling or sample preparation activities are comparable between surveys, the analytical laboratories must be shown to have provided comparable data. This assessment was made by examining data from the natural audit samples. If the analytical data are comparable across regions, the sample preparation can be compared using data from the preparation duplicates. If the preparation data are comparable across regions, then the field sampling can be compared using data from the field duplicates and from validation activities, e.g., aggregation.

A comprehensive discussion on the comparability among the three surveys (NE, SBRP, and Mid-Appalachian) is planned to be presented in the QA report for the Mid-Appalachian Soil Survey.

Section 3

Results and Discussion

The results described in this section are based on the analysis of data values in the official Northeastern verified data base.

Detectability

Data relating to detection limits for contract requirements, instrument readings, and system-wide measurement in the Northeastern survey are presented in Table 3-1.

Two different CRDLs were used for the base cation parameters during analysis of the samples. The reduction in the CRDL from 0.20 to 0.05 mg/L in the case of CA_CL and NA_CL reduced the IDL as much as one order of magnitude. The IDLs exceeded the CRDLs only for CA_CL and NA_CL at the 0.20 mg/L level, whereas all IDLs were lower than their associated CRDLs at the 0.05 mg/L level. The reduction in CRDL for FE_CL2 and AL_CL2 from 0.50 to 0.05 also resulted in a dramatic decrease in the IDL. As expected, the SDLs generally were larger than the IDLs. As no effort was made to distinguish the precision of field duplicates from analyses under different CRDLs, the resulting SDL often fell between the two calculated IDLs. One noteworthy exception to this pattern is CA_CL2 for which a SDL is not appropriate because calcium was added to the soil solution as part of the procedure.

The IDLs also exceeded the CRDLs by an order of magnitude for the CEC parameters. Greater attention should be given to these two parameters in future surveys in order to improve the IDL and consequent data quality. The IDLs were lower than the CRDLs for AC_KCL and AC_BACL but higher for AL_KCL. The SDLs were higher than the IDLs in all cases. It appears that a reduction in the CRDL for AC_KCL would be feasible in future surveys, whereas the AC_BACL procedure should be redesigned in order to improve the IDLs.

The IDLs were lower than the CRDLs for the six extractable iron and aluminum parameters, and, as expected, the SDLs were much larger than the IDLs. This suggests the importance of considering detection limits for the overall measurement system, rather than simply the detection limits for the analytical instrument during the development of data quality objectives for detectability.

The calculated IDLs were lower than the CRDLs for the extractable sulfate and sulfate isotherm parameters. The IDLs have been converted from a solution concentration to a soil concentration for comparison to the SDLs. The SO4_H2O parameter has a SDL that falls between the calculated IDLs that were generated from data analyzed under separate solicitations while SO4_PO4 has a SDL which is larger than both IDLs. As expected, the IDLs and SDLs are larger for SO4_PO4 than for SO4_H2O. Although SDLs were calculated for each of the sulfate isotherm parameters, the only SDL of relevance is that for SO4_0, as sulfate was added to the soil solution for the other isotherms. The increase in SDL from SO4_0 to SO4_32 reflects the concentration dependency of the precision estimates.

The IDL was lower than the CRDL for S_TOT but was higher for both C_TOT and N_TOT. Greater attention should be given to improving the analytical procedures for these parameters. The SDLs were larger than the IDLs for C_TOT and S_TOT, but lower than the IDL for N_TOT. One possible explanation for this is that the contract laboratories may not

Table 3-1. Detection Limits for Contract Requirements, Instrument Readings, and System-Wide Measurement

Parameter	CRDL[a]	Calc IDL[b]	Conv IDL[c]	SDL[d]	%RS>SDL[e]
CA_CL	0.05 mg/L	0.0333 mg/L	0.0043 meq/100g	0.0237 meq/100g	88.5
MG_CL	0.05 "	0.0174 "	0.0037 "	0.0058 "	88.5
K_CL	0.05 "	0.0285 "	0.0019 "	0.0090 "	95.5
NA_CL	0.05 "	0.0343 "	0.0039 "	0.0149 "	71.7
CA_OAC	0.05 mg/L	0.0275 mg/L	0.0036 meq/100g	0.0215 meq/100g	89.5
MG_OAC	0.05 "	0.0278 "	0.0059 "	0.0126 "	83.0
K_OAC	0.05 "	0.0282 "	0.0019 "	0.0163 "	84.4
NA_OAC	0.05 "	0.0279 "	0.0032 "	0.0319 "	44.2
CEC_CL	0.01 meq/L	0.0661[f] meq/L	0.1722 meq/100g	0.6032 meq/100g	92.2
CEC_OAC	0.01 "	0.1086[f] "	0.2172 "	0.8541 "	96.5
AC_KCL	0.25 "	0.0693 "	0.1386 "	0.2400 "	82.1
AC_BACL	0.40 "	0.3374 "	1.0122 "	3.6072 "	78.3
AL_KCL	0.10 mg/L	0.1235 mg/L	0.0274 "	0.1267 "	84.0
CA_CL2	—[g] mg/L	0.0208 mg/L	0.0002 meq/100g	0.0939 meq/100g	99.9
MG_CL2	0.05 "	0.0144 "	0.0002 "	0.0023 "	93.7
K_CL2	0.05 "	0.0258 "	0.0001 "	0.0022 "	93.8
NA_CL2	0.05 "	0.0343 "	0.0003 "	0.0081 "	87.4
FE_CL2	0.05 "	0.0183 "	0.0002 "	0.0014 "	45.2
AL_CL2	0.05 "	0.0295 "	0.0007 "	0.0058 "	71.7
FE_PYP	0.50 mg/L	0.1941 mg/L	0.0020 wt %	0.0200 wt %	92.5
AL_PYP	0.50 "	0.2880 "	0.0029 "	0.0603 "	85.1
FE_AO	0.50 "	0.1972 "	0.0021 "	0.0193 "	96.9
AL_AO	0.50 "	0.2238 "	0.0022 "	0.0457 "	94.6
FE_CD	0.50 "	0.1739 "	0.0006 "	0.0653 "	95.4
AL_CD	0.50 "	0.2697 "	0.0009 "	0.0223 "	97.2
SO4_H2O	0.10 mgS/L	0.0250 mgS/L	0.1669 mgS/kg	1.1905 mgS/kg	99.1
SO4_PO4	0.10 "	0.0725 "	0.6050 "	3.2985 "	90.7
SO4_0	0.10 "	0.0306 "	—	0.1319 "	98.8
C_TOT	0.010 wt %	0.0387 wt %	—	0.0478 wt %	97.1
N_TOT	0.010 "	0.0776 "	—	0.0058 "	88.5
S_TOT	0.010 "	0.0045 "	—	0.0051 "	72.7

[a] Contract-required detection limit.

[b] Calculated instrument detection limit; estimated as three times the pooled standard deviation of a low-level DL-QCCS.

[c] Converted instrument detection limit; based on the specified reporting units.

[d] System detection limit; estimated as three times the pooled standard deviations of the lowest 10 percent of field duplicates; independent of the CRDL.

[e] Percent of routine samples exceeding the system detection limit.

[f] Estimated by averaging laboratory-reported IDLs for incomplete DL-QCCS data.

[g] CRDL reported as standard deviation of ten nonconsecutive blanks.

NOTE: Detection limits were not applicable for the physical parameters, soil pH, and the remainder of the sulfate isotherm parameters.

have used appropriate DL-QCCS. One laboratory used a small amount of a high concentration standard sample for a DL-QCCS. The variability was excessive due to the lack of precision in weighing such a sample. These results were not included in the calculation of the IDLs.

Precision

The following tables, figures, and text are designed to satisfy the requirements of the data users for summary precision estimates of the routine and QA sample data. The audit and duplicate samples represent means and variability for a pair of theoretically identical samples. The routine samples described the heterogeneity of the population plus analytical uncertainty in a set of two to approximately twenty samples. The assessment of precision relates directly to the achievement of intralaboratory within-batch DQOs established in the DDRP QA Plan (Bartz et al., 1987). In most cases, the DQOs have knot values which represent the separation point for the data uncertainty expressed as a standard deviation for low concentrations and as a relative standard deviation in percent for higher concentrations.

The precision data are presented in sequential order of the parameters listed in Table 1-1 of Section 1 of this report. For each of the nine parameter groups, a table of statistics presents the QA and routine sample data below and above the knot for the mineral samples. Organic samples were not included because no DQOs were established for these samples. These tables show the relationship of the QA data to the DQOs.

Two figures are presented for each parameter within each parameter group. The first figure is a plot of the mean and standard deviation of each pair of audit samples from a batch for each of the five audit sample types (Oa, A, Bs, Bw, and C) and their relationship to the DQO for each parameter. The second figure is a plot of the mean and standard deviation of each of the horizon/sampling class groups from the routine samples. The variability seen in the sampling class/horizon data is principally the result of spatial heterogeneity among the population of soils within each group. More specifically, horizons of similarly classified soils in widely separated regions, e.g., Virginia and New York, are commonly dissimilar in soil characteristics. This is due to subtle differences resulting from local soil-forming influences of climate, topography, vegetation, parent material, and time. Also included in this plot are sets of four horizontal lines representing within-batch standard deviations for the field duplicates, preparation duplicates, and natural audit samples, and between-batch standard deviation for the natural audit samples. Each set of lines represents the data uncertainty within the windows that were established by the step function across the total range of concentration. Although the data uncertainty is not always constant within the windows for each type of sample represented, the lines are treated as constants. This latter figure is intended to show the contribution of measurement uncertainty to the overall variability of the routine data.

Additional tables corresponding to the step function statistical procedure for each of the parameters are given in Appendix C as supplemental information for the derivation of the precision data provided in the plots. Appendix D presents data that were sorted according to the sampling class/horizon group and the batch/sample number. These data correspond to routine or QA samples having inordinately high or low values that exert a disproportionate influence on the assessment of data quality. These data are of interest to data users when making evaluations of individual data sets represented in the plots or of individual batches of samples from a given analytical laboratory.

Moisture, Specific Surface, and Particle Size Analyses

The analytical within-batch precision DQO was satisfied for CLAY but not for SAND and SILT, where approximately one third of the samples exceeded the DQO (see Table 3-2). The percentage of sand in the samples from this survey usually was much higher than the percentage of clay. The DQO of 1.0 weight percent for the particle size fractions did not allow much room for error in horizons dominated by either sand, silt, or clay. For the latest DDRP survey, the DQOs for particle size were raised two- or three-fold to account for these dominating particle sizes. For the remaining parameters of this group, precision DQOs were not defined. A general pattern of increasing standard deviation with increased sources of confounded error was found, i.e., the standard deviation from the field duplicate samples exceeded that of the preparation duplicate and natural audit samples. The precision estimates for SAND and SILT remained relatively constant from the preparation duplicates to the field duplicates, despite the increasing sources of error. These analyses were not performed on the organic horizon samples because the mineral soil component for which these analyses were designed were low or absent in the organic soil.

Figures 3-1 through 3-6 are plots of the audit sample data in relation to the DQOs and of the routine sample data in relation to the QA samples. The plots are provided only for the those particle size parameters for which the precision DQOs are defined, i.e., for SAND, SILT, and CLAY. The subfractions of the sand and silt are not included. Appendix E contains the routine data plots for the remaining physical parameters. Supplemental information relating to delta and proportion values is presented in Appendix C, and the identification of inordinate data values is presented in Appendix D.

Table 3-2. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of Moisture, Specific Surface, and Particle Size Analysis

Data set[a]	Parameter	df	SD[b]	DQO[b]	Pairs>DQO n	Pairs>DQO %
AS	MOIST	50	0.1194			
	SP_SUR	50	3.6290[d]			
	SAND	50	1.6070	1.00	16	32.0
	VCOS	50	1.0348			
	COS	50	1.5354			
	MS	50	1.1470			
	FS	50	1.5530			
	VFS	50	1.3860			
	SILT	50	1.4448	1.00	17	34.0
	COSI	50	1.2003			
	FSI	50	1.0023			
	CLAY	50	0.5908	1.00	4	8.0
PD	MOIST	55	0.4266			
	SP_SUR	55	3.2045[d]			
	SAND	55	2.5062		14	25.5
	VCOS	54	1.2852			
	COS	55	1.0407			
	MS	55	1.7333			
	FS	55	2.0418			
	VFS	55	1.3927			
	SILT	55	2.6272		14	25.5
	COSI	55	2.1427			
	FSI	55	0.9944			
	CLAY	55	0.5594		5	9.1
FD	MOIST	241	0.6384			
	SP_SUR	241	5.4592[d]			
	SAND	241	2.4530		94	39.0
	VCOS	240	1.3994			
	COS	241	1.5498			
	MS	241	0.9857			
	FS	241	1.2728			
	VFS	241	1.1540			
	SILT	241	2.2055		92	38.2
	COSI	241	1.7209			
	FSI	241	1.5314			
	CLAY	240	1.1528		30	12.5
S/H	MOIST	1077	1.3621			
	SP_SUR	1076	28.1681[d]			
	SAND	1075	12.7859			
	VCOS	1076	5.7177			
	COS	1076	6.1556			
	MS	1076	5.7972			
	FS	1076	7.0470			
	VFS	1076	5.9346			
	SILT	1075	10.6731			
	COSI	1076	6.0284			
	FSI	1076	6.9087			
	CLAY	1075	4.4452			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

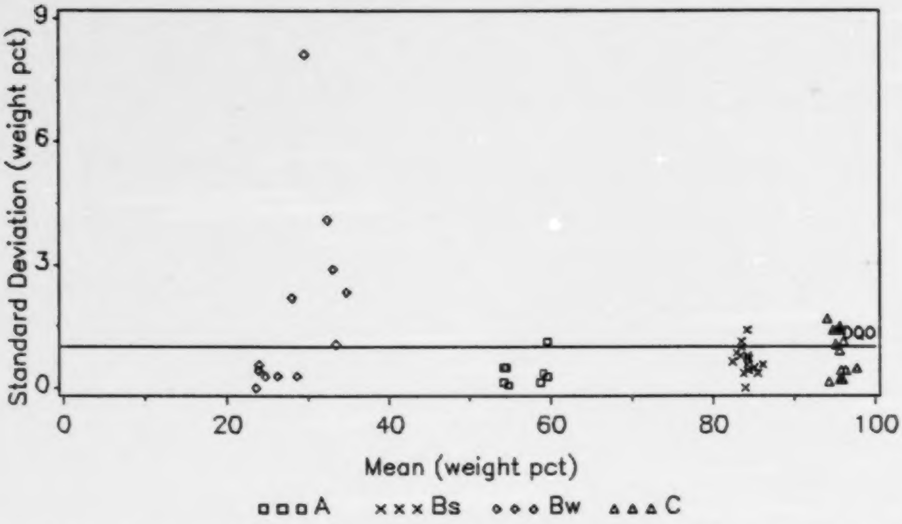
[b] Degrees of freedom.

[c] Standard deviations for mineral soil samples, expressed in weight percent.

[d] Reporting unit for SP_SUR is m^2/g.

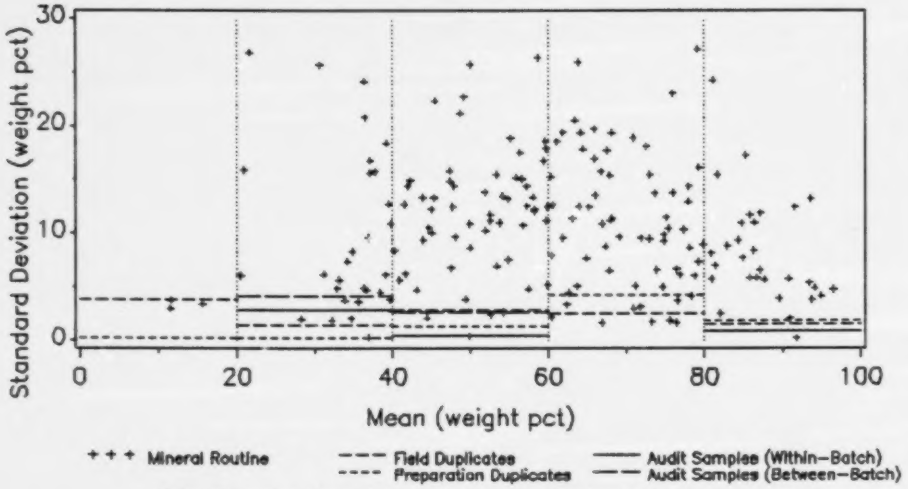
SAND

Total Sand



Natural Audit Samples

Figure 3-1. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SAND.



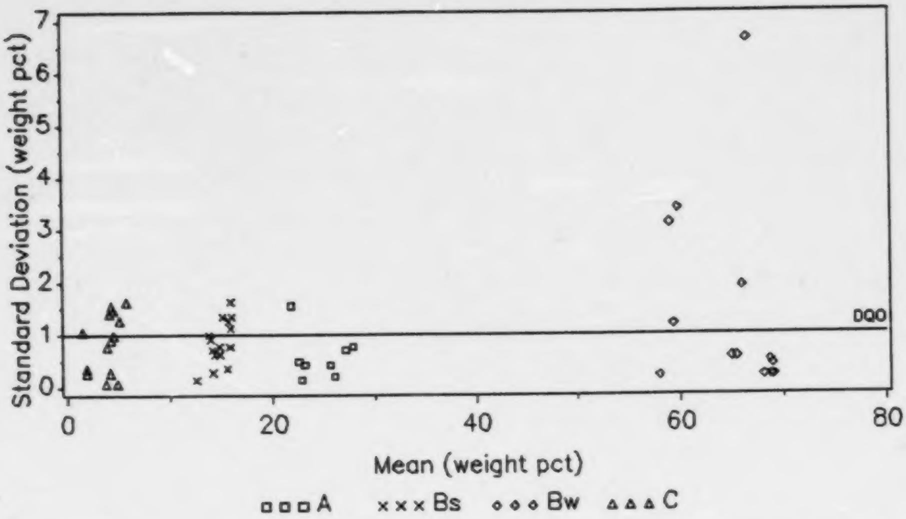
Routine Samples

Note: Four mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-2. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SAND.

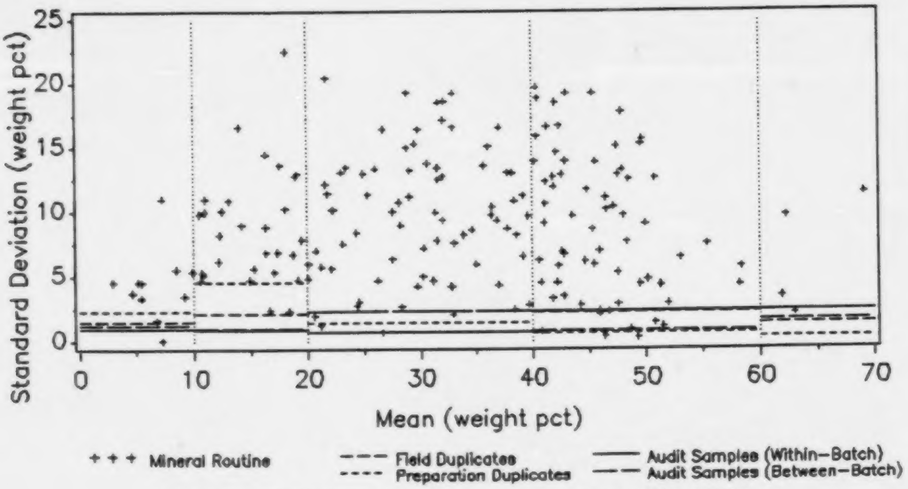
SILT

Total Silt



Natural Audit Samples

Figure 3-3. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SILT.



Routine Samples

Note: Five mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-4. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SILT.

CLAY

Total Clay

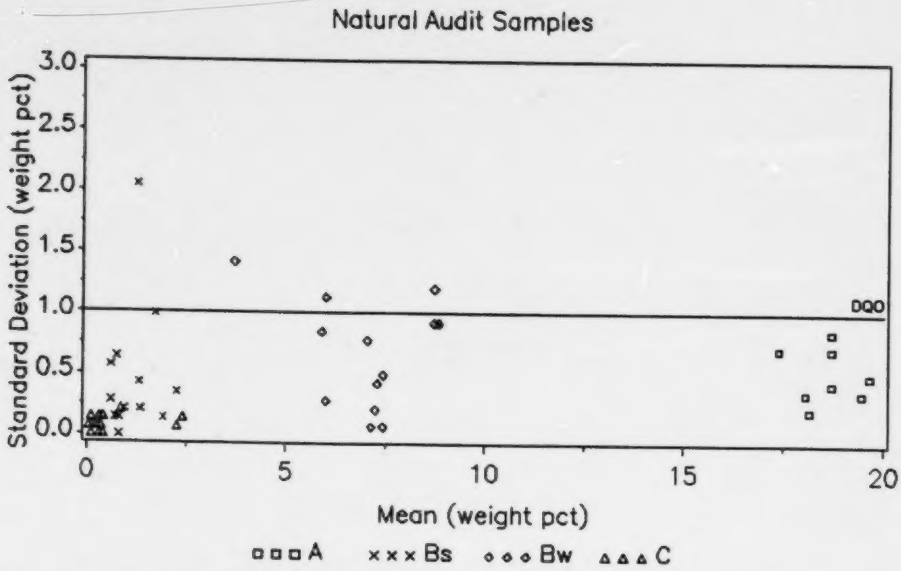
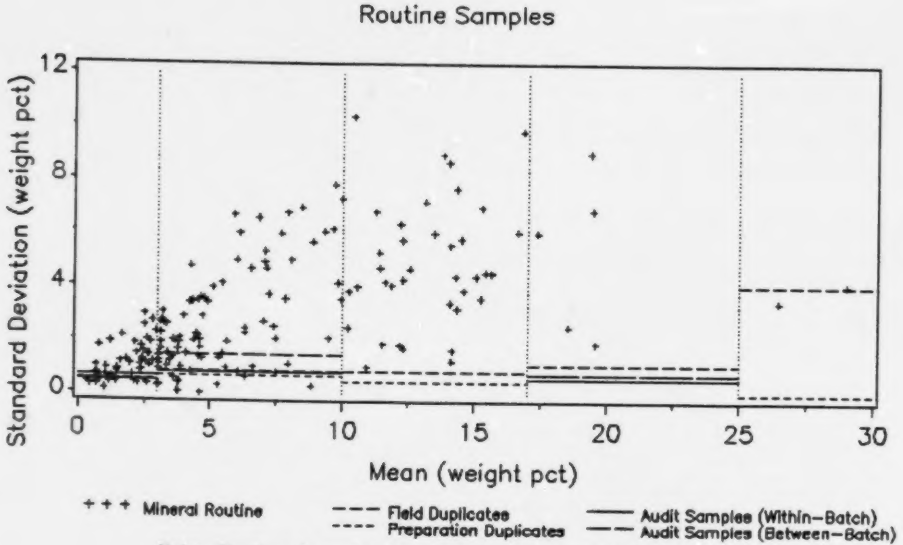


Figure 3-5. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for CLAY.



Note: Six mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-6. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for CLAY.

Soil pH

The analytical within-batch precision DQO was satisfied for each of the pH parameters (see Table 3-3). A general pattern of increasing standard deviation with increased sources of confounded error was maintained for PH_002M only. For pH_H20, the standard deviation showed a slight change over the measured pH range and it was necessary to fit the step function to the data. Unlike most of the other soil chemical parameters, the error variances for PH_002M and PH_01M were constant for the entire ranges of concentration.

Figures 3-7 through 3-12 are plots of the audit sample data in relation to the DQOs and of the routine sample data in relation to the QA samples. Supplemental information regarding delta and proportion values is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-3. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of the pH Parameters

Data set[a]	Parameter	df[b]	SD[c] pH	DQO[c] pH	Pairs>DQO	
					n	%
AS	PH_H2O	50	0.0771	0.15	1	2.0
	PH_002M	50	0.0392	0.15	1	2.0
	PH_01M	50	0.1422	0.15	4	8.0
PD	PH_H2O	55	0.1287		4	7.3
	PH_002M	54	0.0423		1	1.8
	PH_01M	55	0.0315		0	0.0
FD	PH_H2O	241	0.0924		18	7.5
	PH_002M	241	0.0644		6	2.5
	PH_01M	241	0.0925		12	5.0
S/H	PH_H2O	1077	0.4705			
	PH_002M	1076	0.3989			
	PH_01M	1077	0.4064			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations for mineral soil samples, expressed in pH reporting units.

PH_H2O

pH in Deionized Water

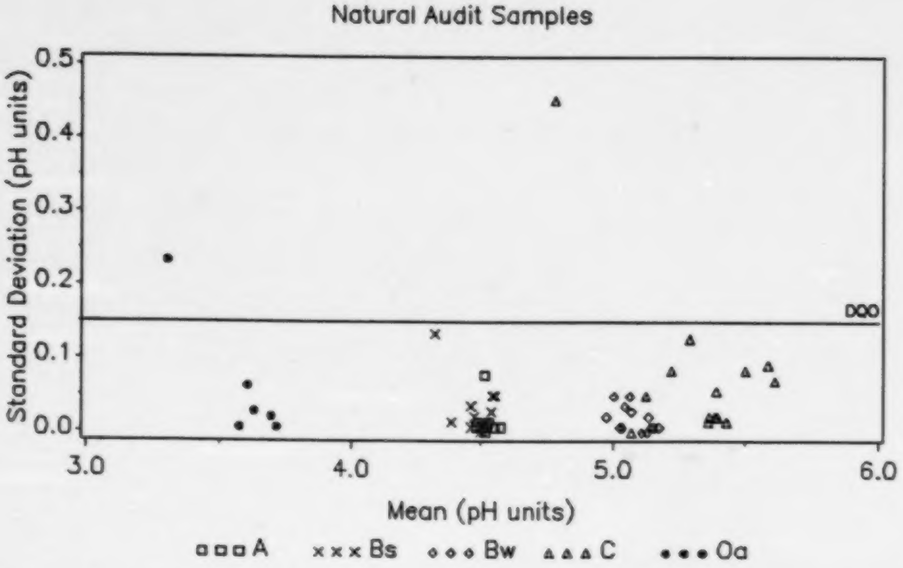
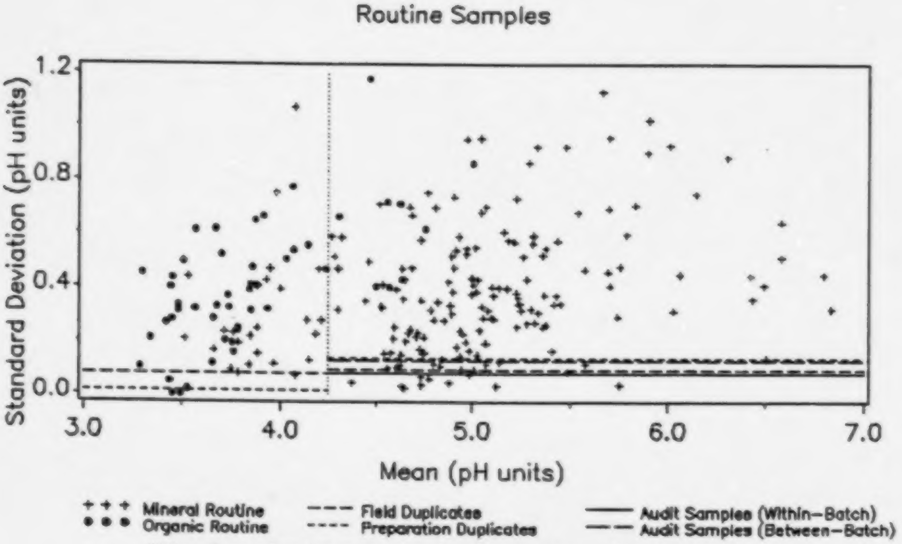

Natural Audit Samples

Figure 3-7. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for PH_H2O.


Routine Samples

Note: Three mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-8. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for PH_H2O.

PH_002M

pH in 0.002M Calcium Chloride

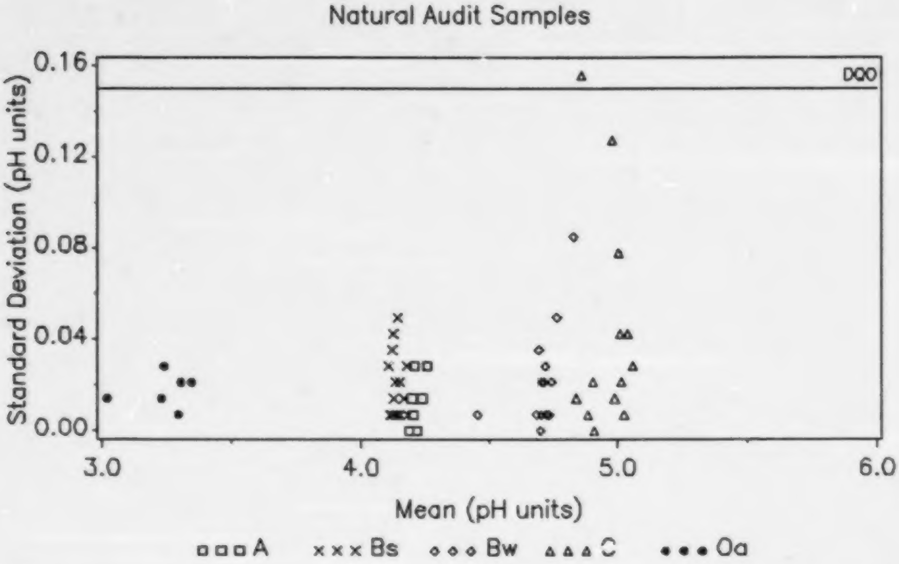
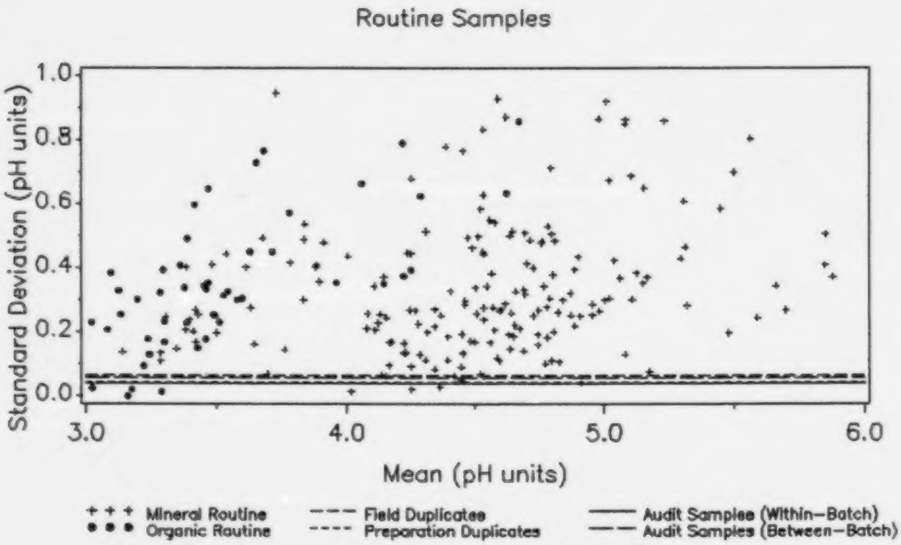


Figure 3-9. **Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for PH_002M.**



Note: Three mineral, two organic sampling class/horizon groups exceed plot boundaries.

Figure 3-10. **Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for PH_002M.**

PH_01M

pH in 0.01M Calcium Chloride

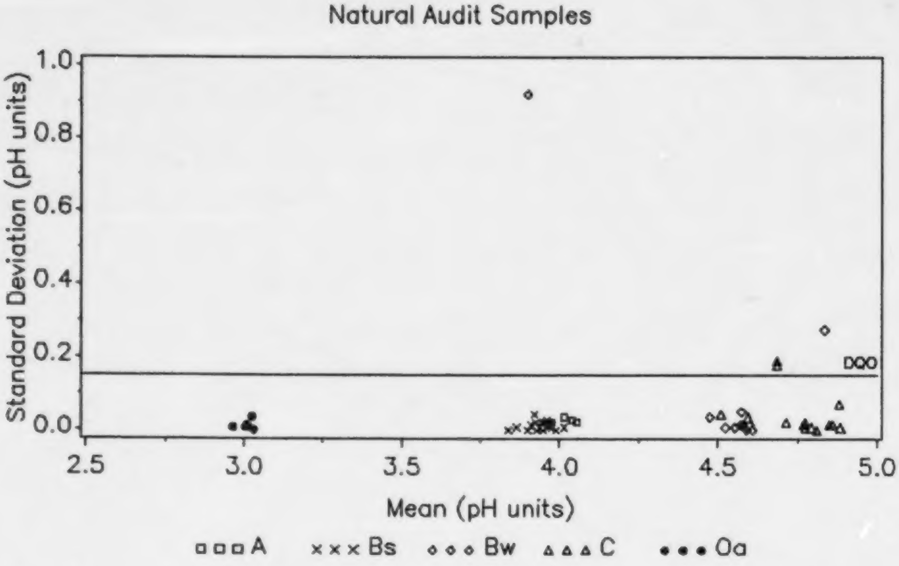
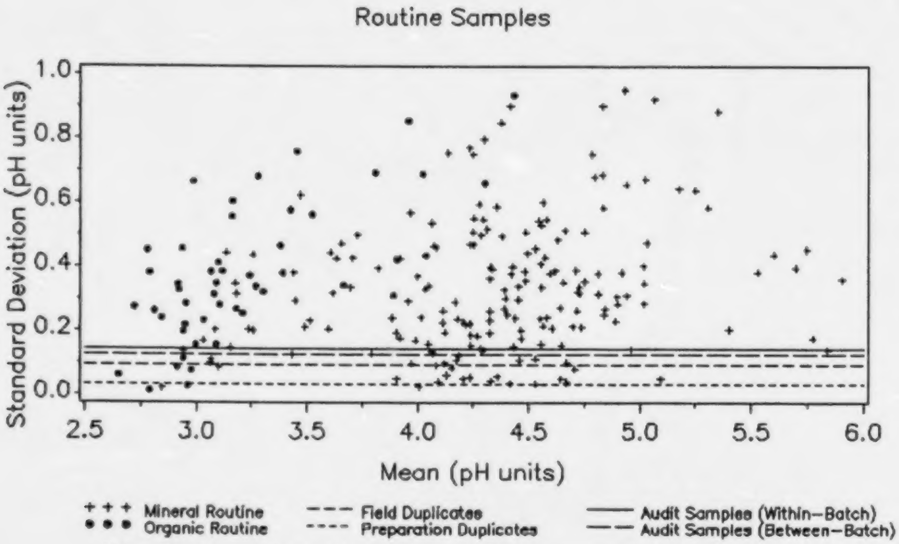

Natural Audit Samples

Figure 3-11. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for PH_01M.


Routine Samples

Note: Four mineral, one organic sampling class/horizon groups exceed plot boundaries.

Figure 3-12. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for PH_01M.

Exchangeable Cations in Ammonium Chloride

The analytical within-batch precision DQOs were satisfied for all of the cations in ammonium chloride except for CA_CL below the knot (see Table 3-4). The inordinate effect of data from 3 of the 16 audit sample pairs in the lower tier prevented this parameter from satisfying the DQO.

There was not a general trend of increasing standard deviation with increased sources of confounded error. The precision estimates for the preparation duplicates were generally lower than those for the audit samples and the field duplicates. For the QA samples below the knot, MG_CL had the highest precision and CA_CL had the lowest precision. Above the knot, there was a general trend of increasing standard deviation with increasing sources of confounding error. For the QA samples above the knot, K_CL had the highest precision and CA_CL had the lowest precision.

Figures 3-13 through 3-20 are the plots of the audit sample data in relation to the DQOs and of the routine sample data in relation to the QA samples. Supplemental information relating to the delta values is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-4. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of the Exchangeable Cations in Ammonium Chloride

Data set[a]	Parameter	Below the knot[c]					Above the knot[c]				
			SD	DQO	Pairs>DQO			RSD	DQO	Pairs>DQO	
		df[b]	– meq/100g –		n	%	df	%	%	n	%
AS	CA_CL	16	0.0587	0.03	3	18.8	34	12.4	15	6	17.6
	MG_CL	41	0.0086	0.03	0	0.0	8	10.4	15	1	12.5
	K_CL	42	0.0066	0.03	0	0.0	8	4.5	15	0	0.0
	NA_CL	44	0.0244	0.03	2	4.5	•	•	15	•	•
PD	CA_CL	32	0.0232		3	9.4	23	26.2		2	8.7
	MG_CL	37	0.0062		0	0.0	15	9.0		2	13.3
	K_CL	53	0.0132		2	3.8	1	4.9		0	0.0
	NA_CL	49	0.0145		3	6.1	1	5.0		0	0.0
FD	CA_CL	135	0.0243		22	16.2	103	17.1		21	20.4
	MG_CL	174	0.0120		7	4.0	52	24.1		7	13.5
	K_CL	223	0.0114		12	5.4	16	22.4		3	18.8
	NA_CL	215	0.0239		16	7.4	7	12.9		1	14.3
S/H	CA_CL	417	0.1477				659	138.7			
	MG_CL	730	0.0684				345	301.0			
	K_CL	1044	0.0513				32	87.6			
	NA_CL	1016	0.0495				34	316.9			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in reporting units and percent, respectively, for mineral soil samples below and above the knot point of 0.20 meq/100g; a dot signifies a lack of data occupying that range.

CA_CL

Exchangeable Calcium in Ammonium Chloride

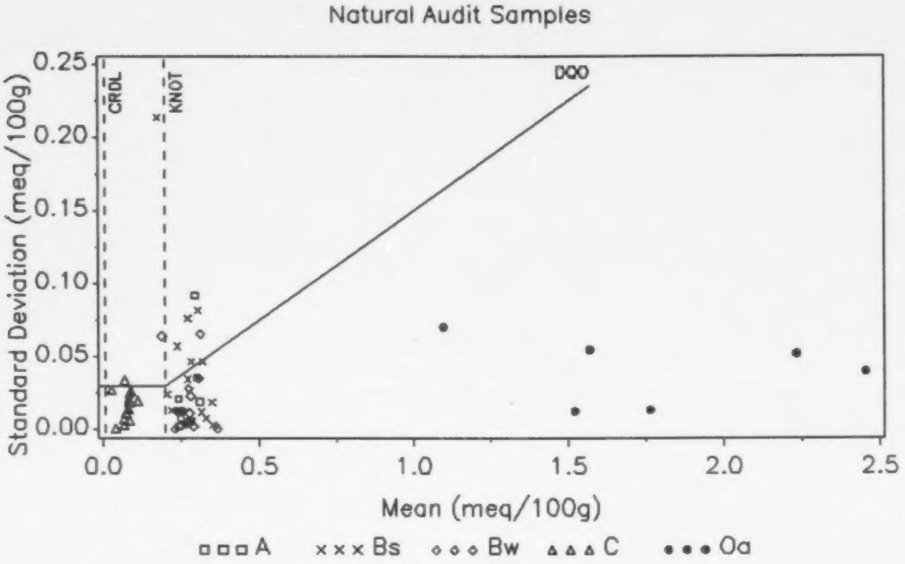
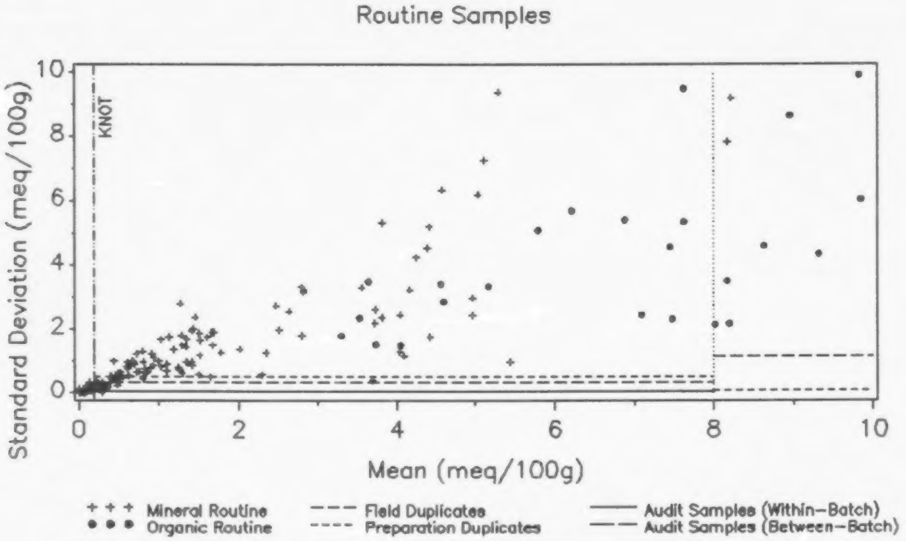

Natural Audit Samples

Figure 3-13. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for CA_CL.


Routine Samples

Note: Three mineral, twenty six organic sampling class/horizon groups exceed plot boundaries.

Figure 3-14. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for CA_CL.

MG_CL

Exchangeable Magnesium in Ammonium Chloride

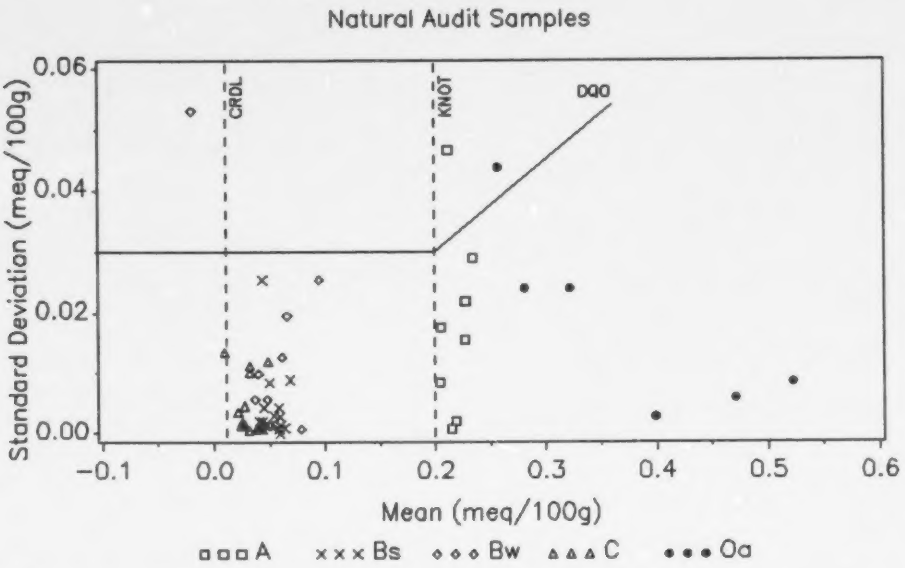
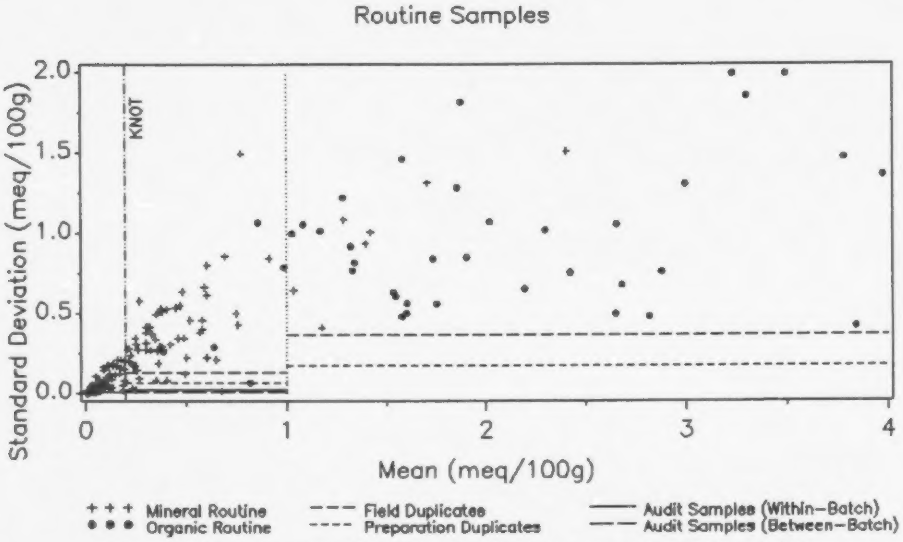
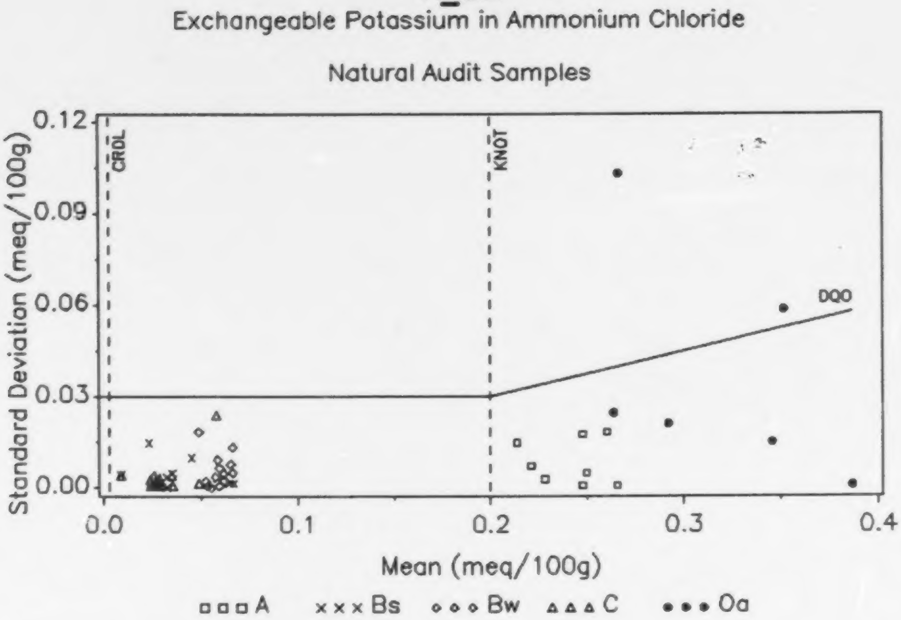


Figure 3-15. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for MG_CL.



Note: Six mineral, eleven organic sampling class/horizon groups exceed plot boundaries.

Figure 3-16. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for MG_CL.

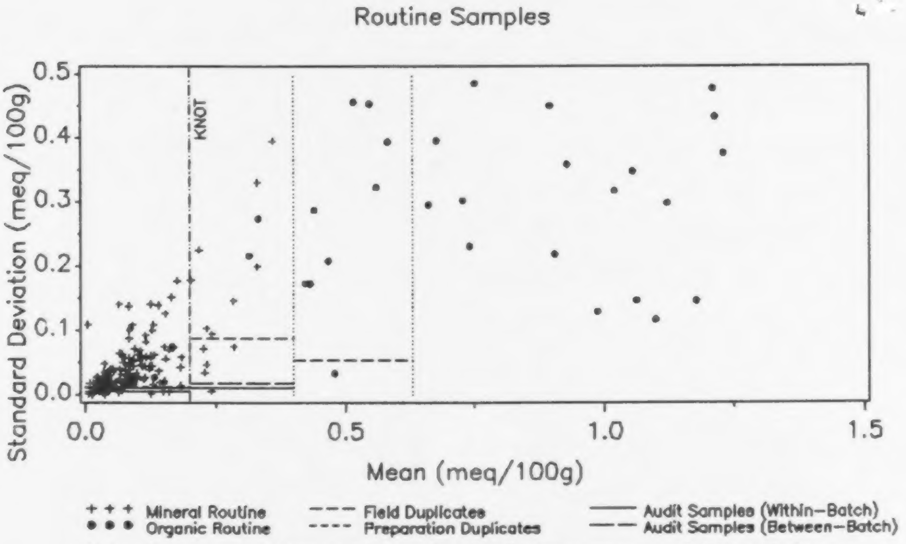


K_CL

Exchangeable Potassium in Ammonium Chloride

Natural Audit Samples

Figure 3-17. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for K_CL.



Routine Samples

Note: One mineral, eighteen organic sampling class/horizon groups exceed plot boundaries.

Figure 3-18. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for K_CL.

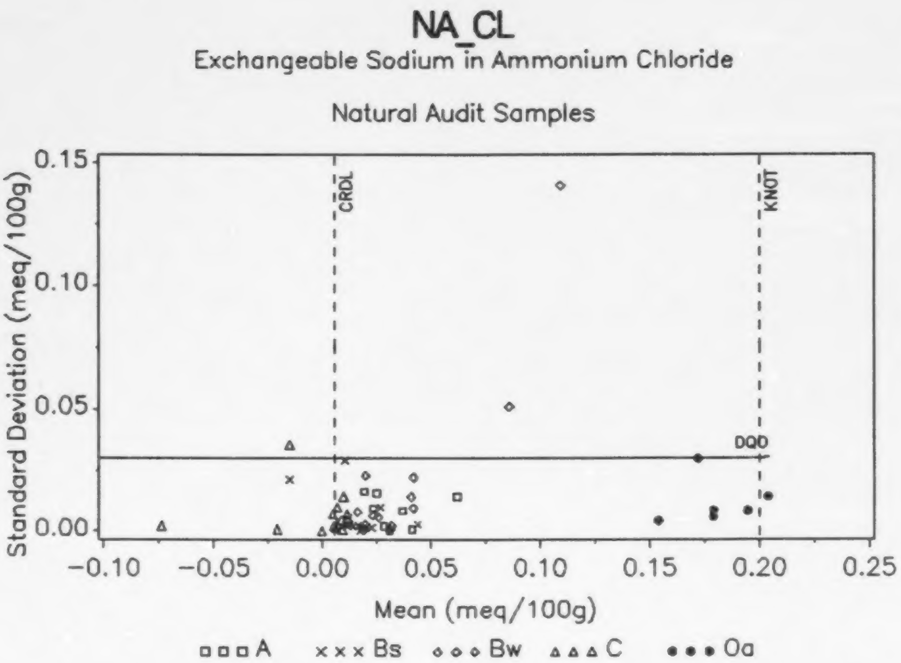
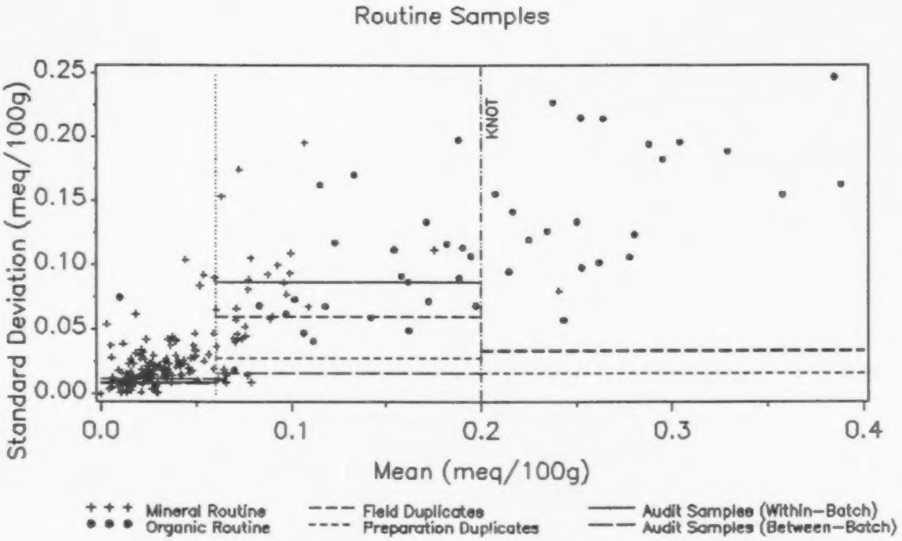


Figure 3-19. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for NA_CL.



Note: Five mineral, five organic sampling class/horizon groups exceed plot boundaries.

Figure 3-20. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for NA_CL.

Exchangeable Cations in Ammonium Acetate

The analytical within-batch precision DQOs were satisfied for the exchangeable cations in ammonium acetate. For CA_OAC, however, 32 percent of the audit sample pairs below the knot and 26 percent above the knot were higher than the DQO (see Table 3-5). A general pattern of increasing standard deviation with increased sources of confounded error was maintained except with the preparation duplicates for CA_OAC and MG_OAC, where the standard error from the preparation duplicates slightly exceeds that of the field duplicates for the lower tier.

For the QA samples below the knot, K_OAC had the highest precision and CA_OAC had the lowest precision. Above the knot, K_OAC had the highest precision and MG_OAC had the lowest precision.

Figures 3-21 through 3-28 are plots of the audit sample data in relation to the DQOs and of the routine sample data in relation to the QA samples. Supplemental information relating to the delta and proportion values presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

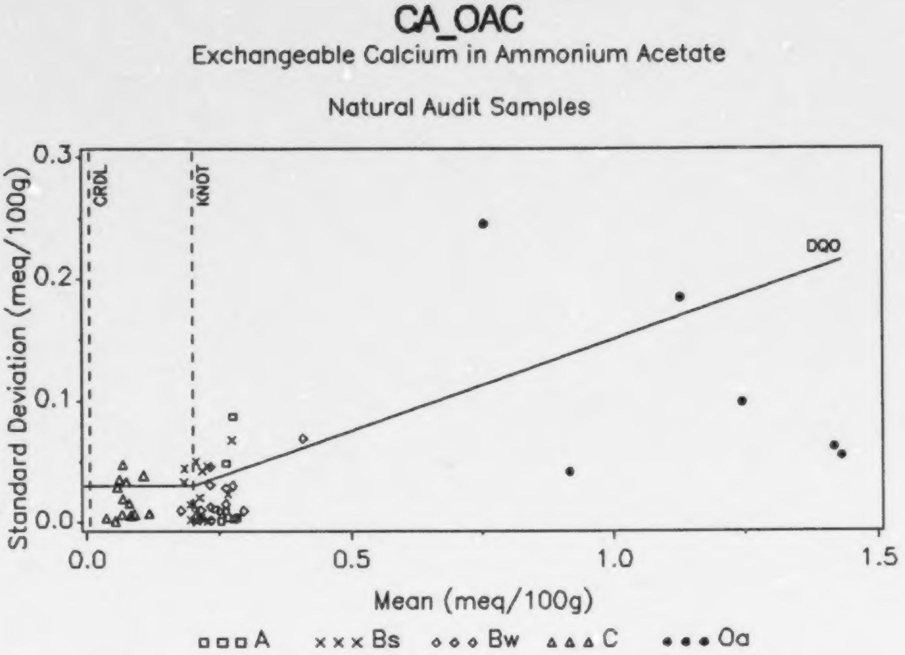
Table 3-5. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of the Exchangeable Cations in Ammonium Acetate

		Below the knot[c]					Above the knot[c]				
Data set[a]	Parameter	df[b]	SD – meq/100g –	DQO – meq/100g –	Pairs>DQO n	Pairs>DQO %	df	RSD %	DQO %	Pairs>DQO n	Pairs>DQO %
AS	CA_OAC	19	0.0245	0.03	6	31.6	31	13.1	15	8	25.8
	MG_OAC	42	0.0105	0.03	1	2.4	7	12.0	15	1	14.3
	K_OAC	42	0.0065	0.03	0	0.0	8	6.4	15	1	12.5
	NA_OAC	43	0.0134	0.03	1	2.3	•	•	15	•	•
PD	CA_OAC	31	0.0247		4	12.9	22	38.0		7	31.8
	MG_OAC	38	0.0293		2	5.3	14	77.4		2	14.3
	K_OAC	52	0.0110		2	3.8	1	1.6		0	0.0
	NA_OAC	48	0.0132		4	8.3	1	2.1		0	0.0
FD	CA_OAC	132	0.0222		14	10.6	103	55.2		23	22.3
	MG_OAC	182	0.0152		9	4.9	52	98.4		8	15.4
	K_OAC	219	0.0118		6	2.7	18	17.3		3	16.7
	NA_OAC	208	0.0175		13	6.2	11	104.8		5	45.5
S/H	CA_OAC	419	0.1371				657	146.5			
	MG_OAC	744	0.0685				332	138.2			
	K_OAC	1044	0.0556				32	88.1			
	NA_OAC	1051	0.0541				17	283.6			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

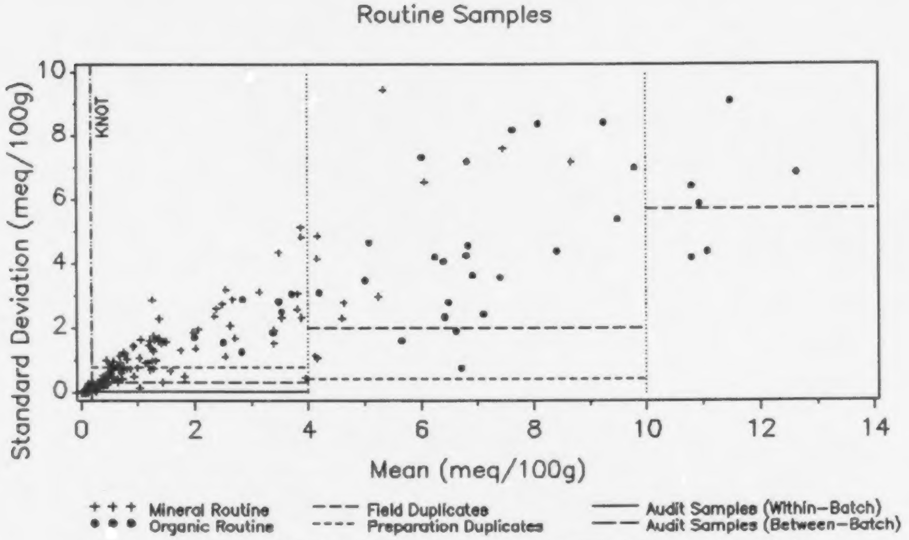
[c] Standard deviations and relative standard deviations expressed in reporting units and percent, respectively, for mineral soil samples below and above the knot point of 0.20 meq/100g; a dot signifies a lack of data occupying that range.


CA_OAC

Exchangeable Calcium in Ammonium Acetate

Natural Audit Samples

Figure 3-21. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for CA_OAC.


Routine Samples

Note: Two mineral, thirteen organic sampling class/horizon groups exceed plot boundaries.

Figure 3-22. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for CA_OAC.

MG_OAC

Exchangeable Magnesium in Ammonium Acetate

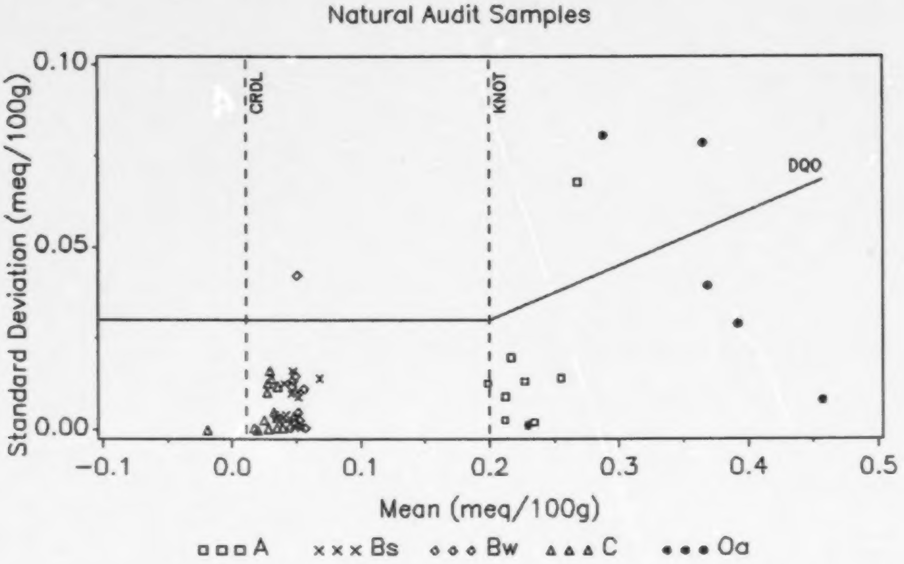
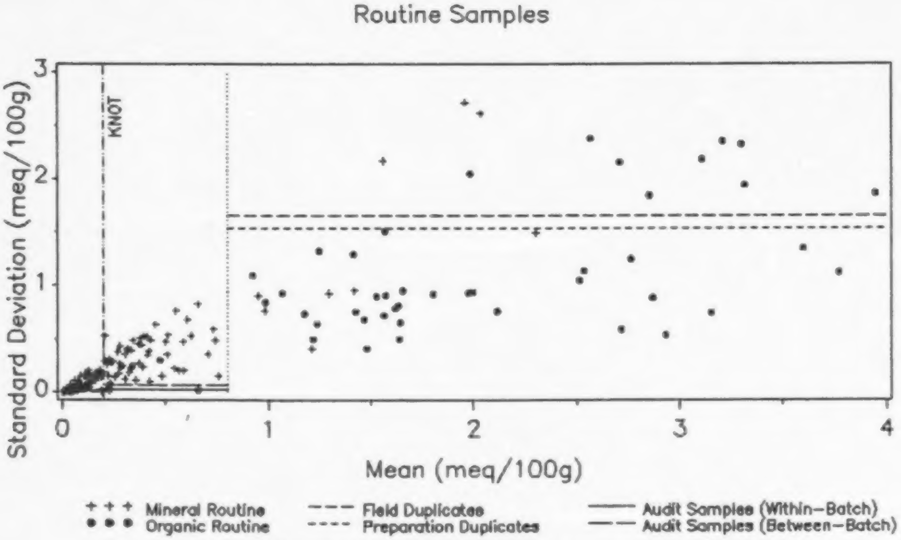
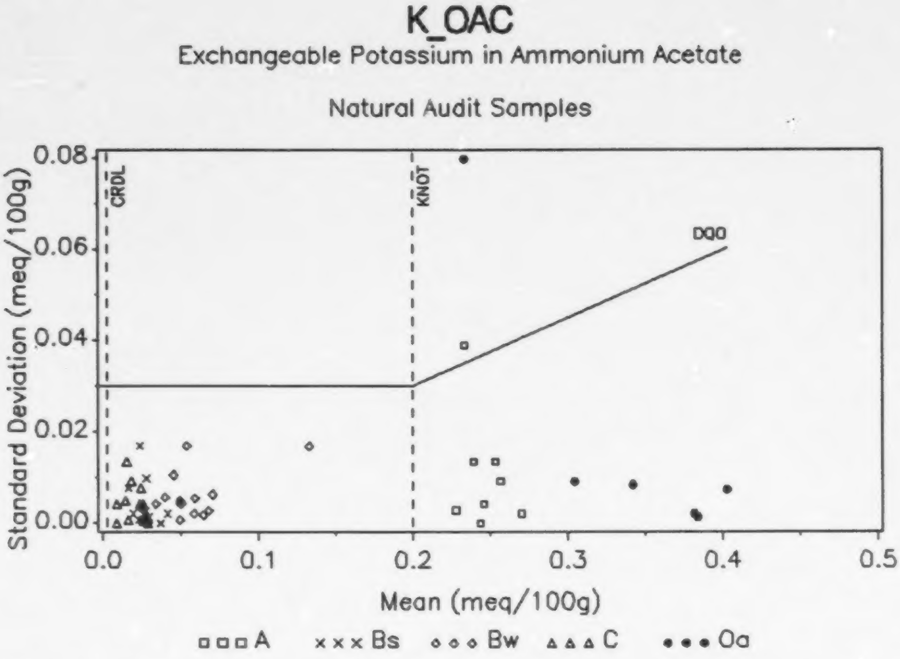


Figure 3-23. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for MG_OAC.



Note: Three mineral, five organic sampling class/horizon groups exceed plot boundaries.

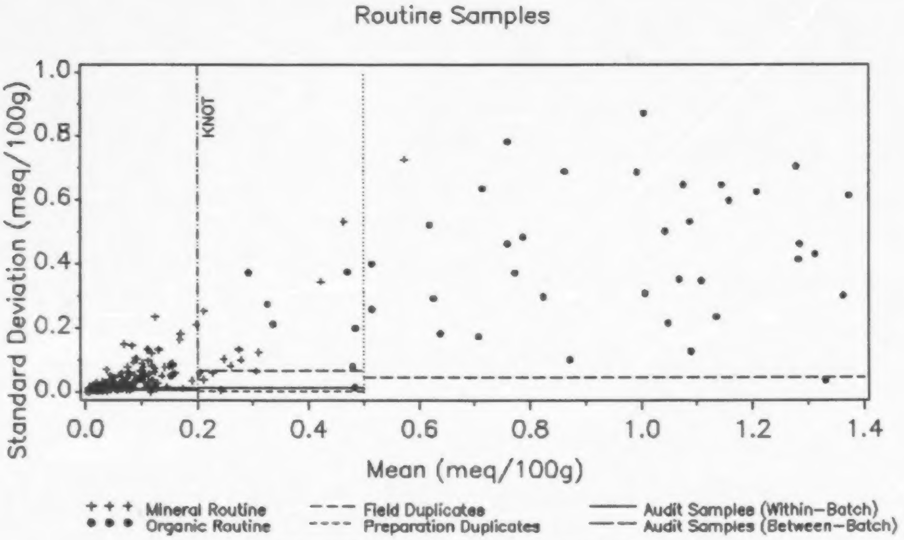
Figure 3-24. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for MG_OAC.


K_OAC

Exchangeable Potassium in Ammonium Acetate

Natural Audit Samples

Figure 3-25. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for K_OAC.


Routine Samples

Note: Six organic sampling class/horizon groups exceed plot boundaries.

Figure 3-26. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for K_OAC.

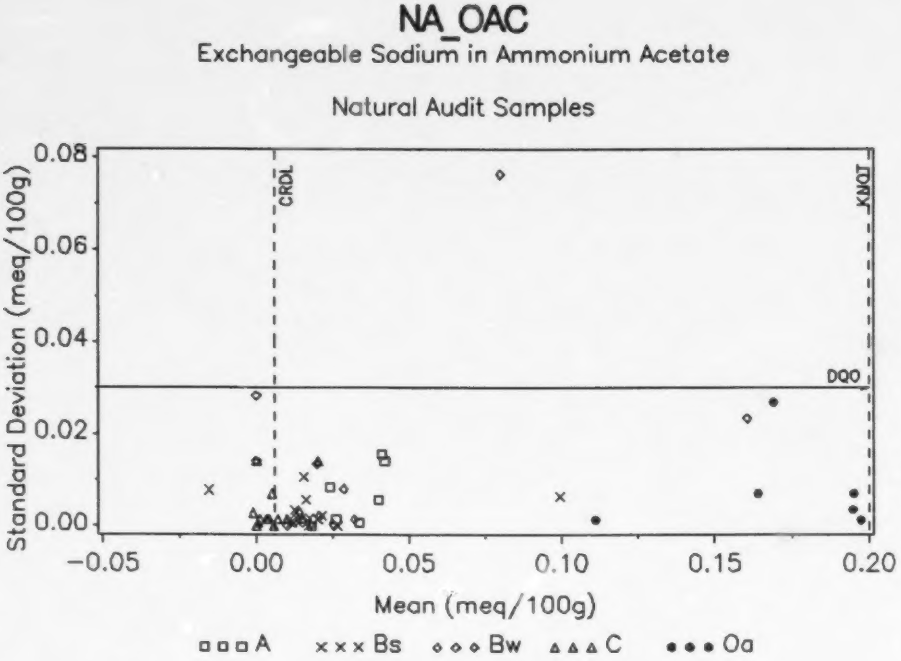
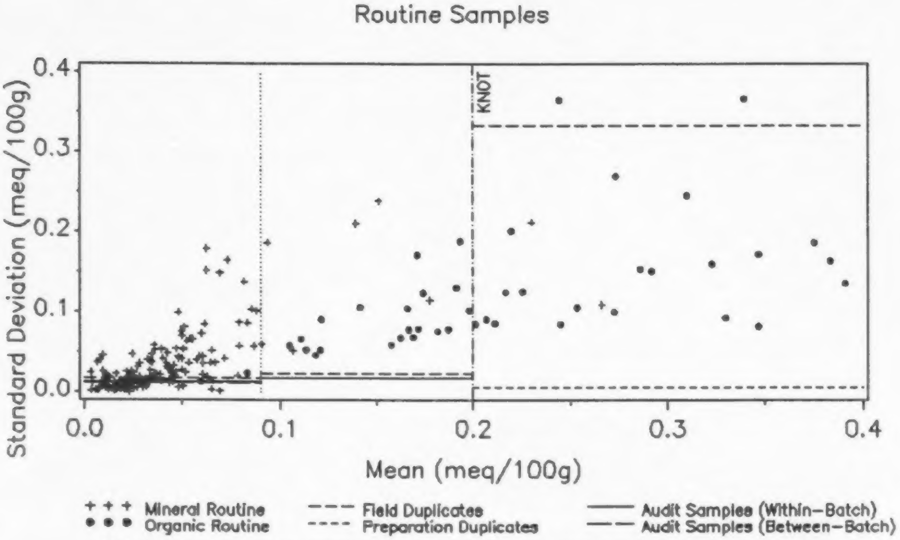


Figure 3-27. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for NA_OAC.



Note: Four mineral, five organic sampling class/horizon groups exceed plot boundaries.

Figure 3-28. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for NA_OAC.

Cation Exchange Capacity and Exchangeable Acidity

The analytical within-batch precision DQOs were satisfied for all parameters in this group except for AC_BACL below the knot, where the standard error is only slightly higher than the DQO (see Table 3-6). Four of the 12 audit pairs below the knot were higher than the DQO.

Both below and above the knot, there was not a clearly defined trend of increasing standard deviation with increased sources of confounded error for the CEC parameters. For the QA samples both below and above the knot, AC_KCL had the highest precision overall. AC_BACL had the lowest precision below the knot and CEC_OAC had the lowest precision above the knot.

Figures 3-29 through 3-38 are plots of the audit sample data in relation to the DQOs and the of routine sample data in relation to the QA samples. Supplemental information relating to the delta and proportion values is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-6. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of Cation Exchange Capacity and Exchangeable Acidity

		Below the knot[c]					Above the knot[c]				
			SD	DQO	Pairs>DQO			RSD	DQO	Pairs>DQO	
Data set[a]	Parameter	df[b]	– meq/100g –		n	%	df	%	%	n	%
AS	CEC_CL	14	0.2223	0.25	2	14.3	36	8.2	10	4	11.1
	CEC_OAC	14	0.0919	0.25	0	0.0	36	5.7	10	3	8.3
	AC_KCL	27	0.1069	0.50	0	0.0	23	5.6	20	0	0.0
	AC_BACL	12	0.6546	0.50	4	33.3	37	8.7	20	1	2.7
	AL_KCL	29	0.1069	0.50	0	0.0	20	15.3	20	1	5.0
PD	CEC_CL	25	0.4765		5	20.0	30	17.4		8	26.7
	CEC_OAC	12	0.4441		4	33.3	43	19.1		12	27.9
	AC_KCL	42	0.2349		2	4.8	9	7.9		1	11.1
	AC_BACL	14	0.9914		9	64.3	40	23.4		15	37.5
	AL_KCL	46	0.2565		2	4.3	5	17.5		1	20.0
FD	CEC_CL	64	0.2464		12	18.8	177	16.7		48	27.1
	CEC_OAC	30	0.2772		8	26.7	211	26.2		47	22.3
	AC_KCL	156	0.2496		5	3.2	78	21.7		5	6.4
	AC_BACL	21	1.2406		11	52.4	214	14.9		48	22.4
	AL_KCL	174	0.3951		6	3.4	66	16.3		4	6.1
S/H	CEC_CL	276	1.0380				800	61.1			
	CEC_OAC	119	1.2758				956	67.5			
	AC_KCL	749	0.9934				324	61.3			
	AC_BACL	77	2.2269				988	64.1			
	AL_KCL	803	0.8832				272	62.6			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in reporting units and percent, respectively, for mineral soil samples below and above the knot point of 2.5 meq/100g; a dot signifies a lack of data occupying that range.

CEC_CL

Cation Exchange Capacity by Ammonium Chloride

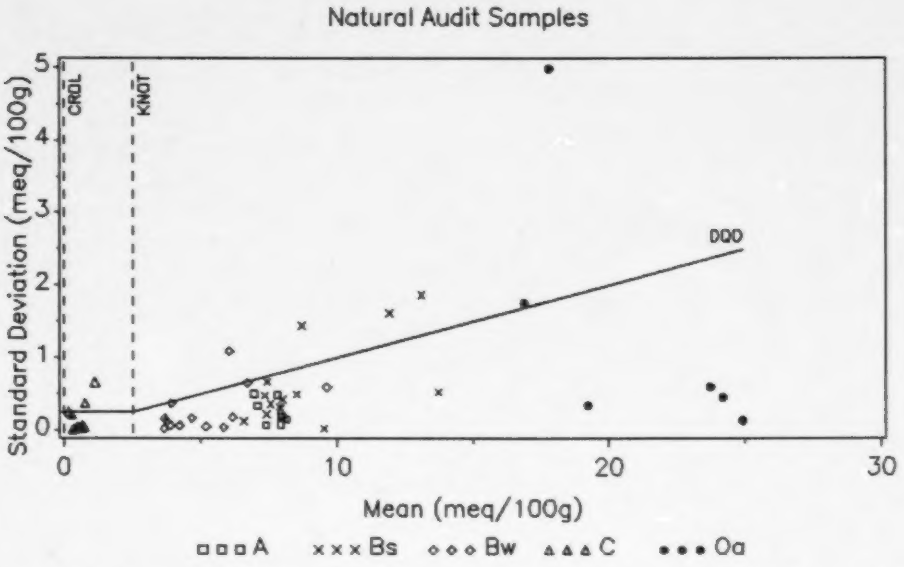
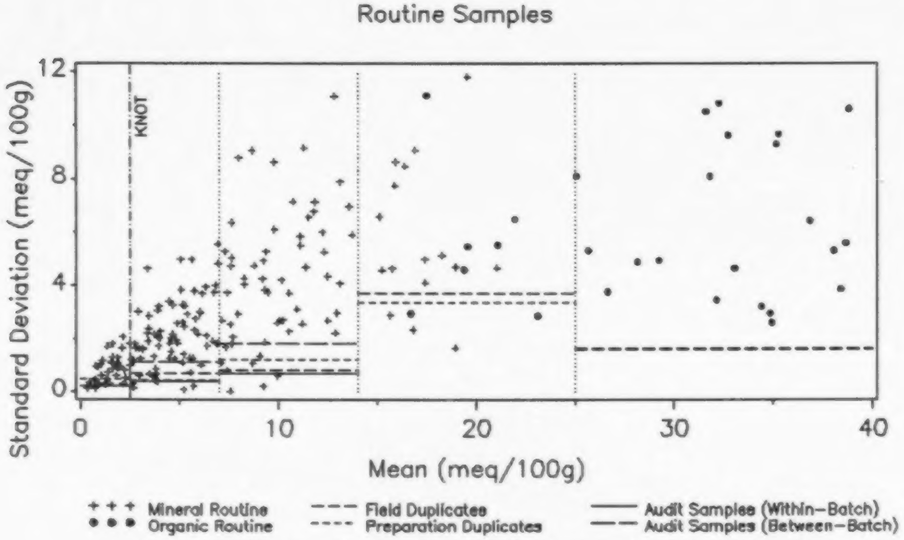


Figure 3-29. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for CEC_CL.



Note: Twenty two organic sampling class/horizon groups exceed plot boundaries.

Figure 3-29. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for CEC_CL.

CEC_OAC

Cation Exchange Capacity by Ammonium Acetate

Natural Audit Samples

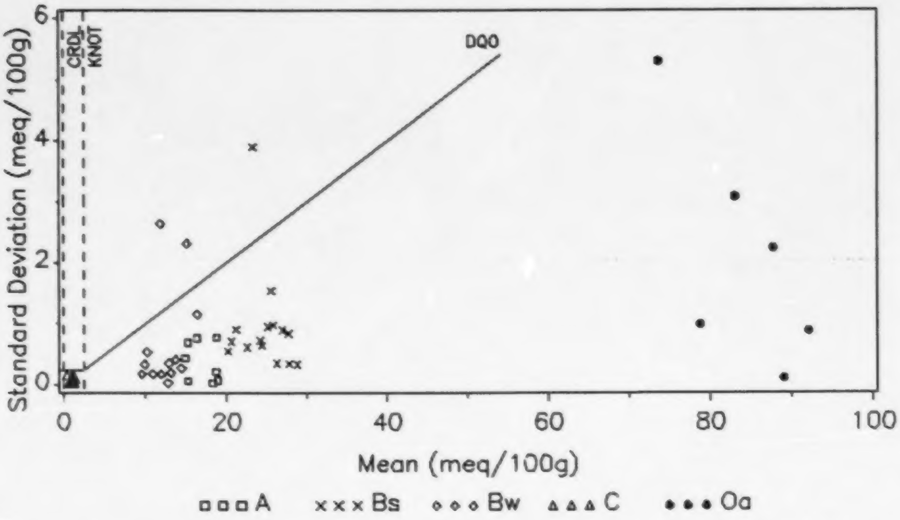
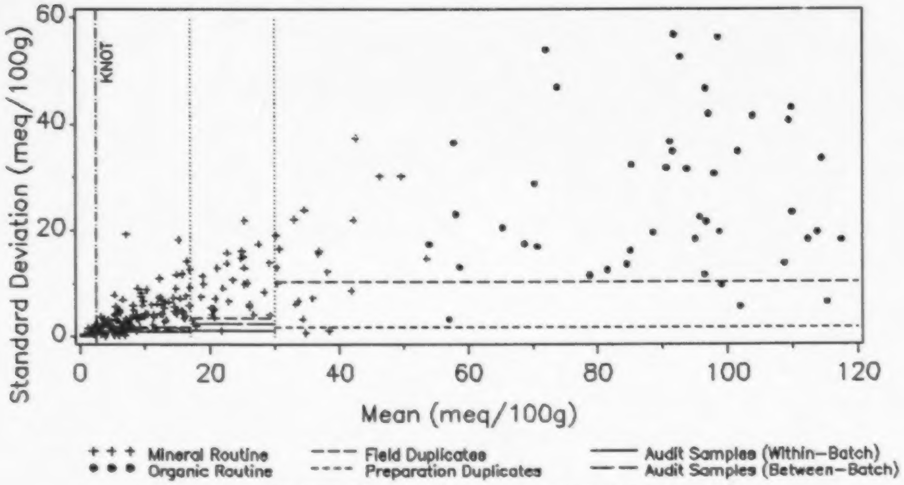


Figure 3-31. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for CEC_OAC.

Routine Samples



Note: Four organic sampling class/horizon groups exceed plot boundaries.

Figure 3-32. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for CEC_OAC.

AC_KCL

Exchangeable Acidity in Potassium Chloride

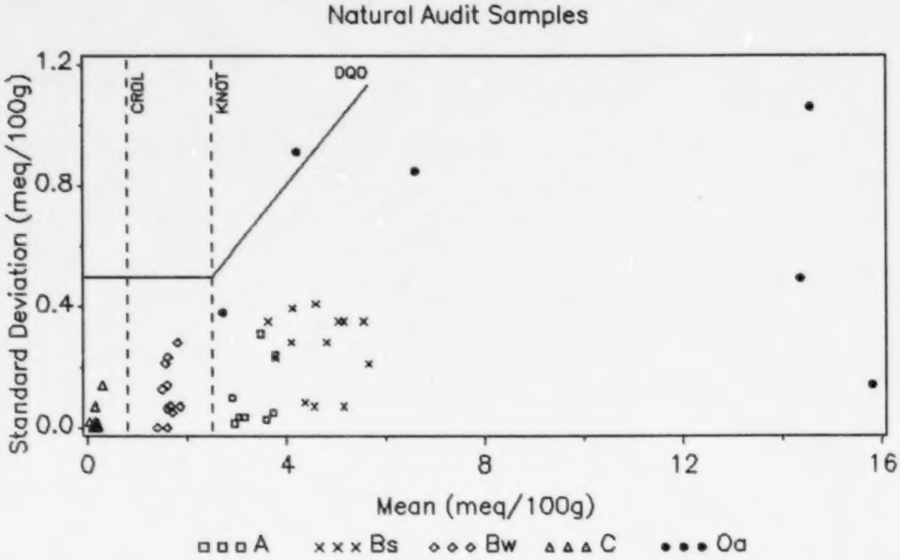
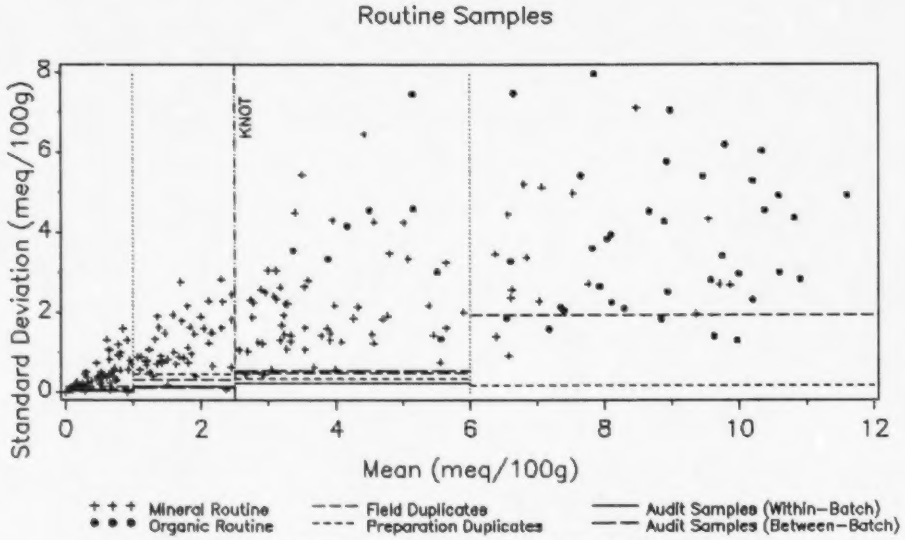


Figure 3-33. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for AC_KCL.



Note: Six organic sampling class/horizon groups exceed plot boundaries.

Figure 3-34. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for AC_KCL.

AC_BACL

Exchangeable Acidity in Barium Chloride Triethanolamine

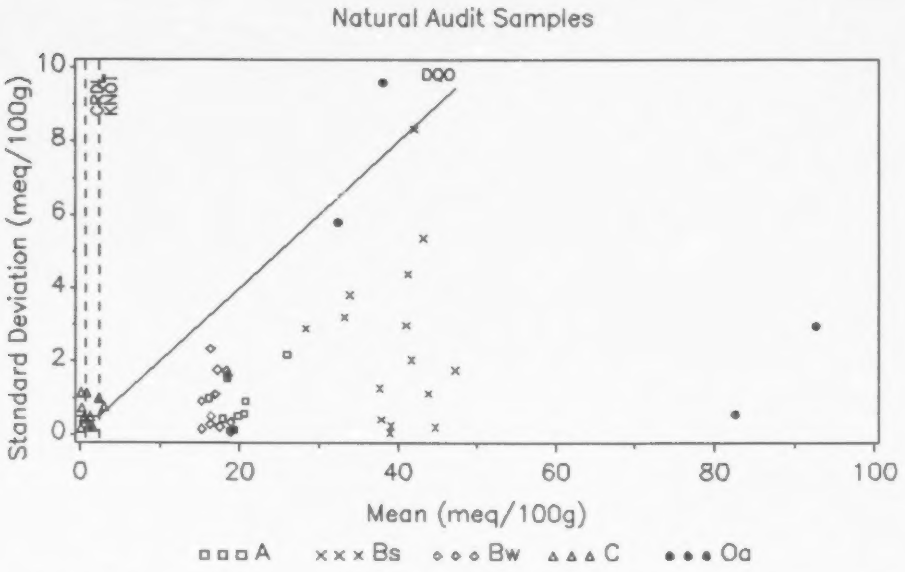
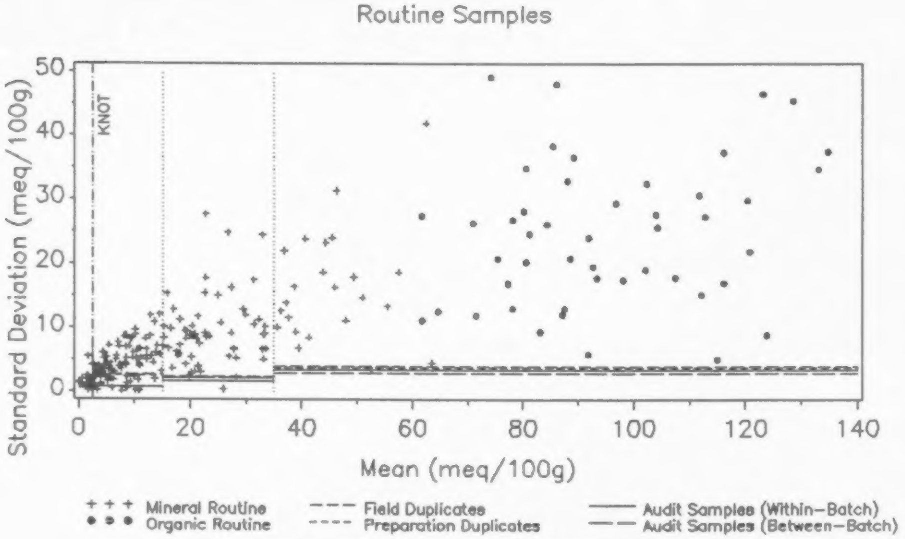


Figure 3-35. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for AC_BACL.



Note: Two organic sampling class/horizon groups exceed plot boundaries.

Figure 3-36. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for AC_BACL.

AL_KCL

Exchangeable Aluminum in Potassium Chloride

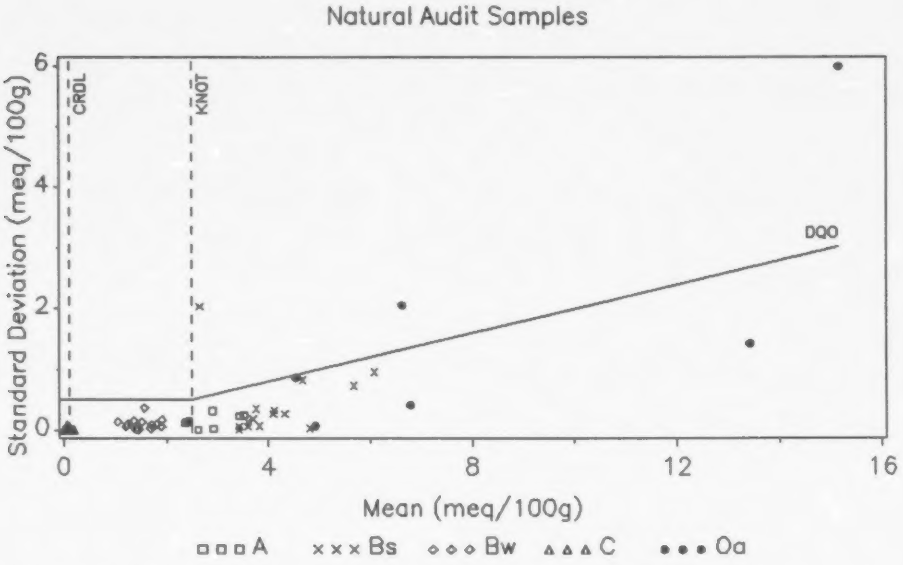
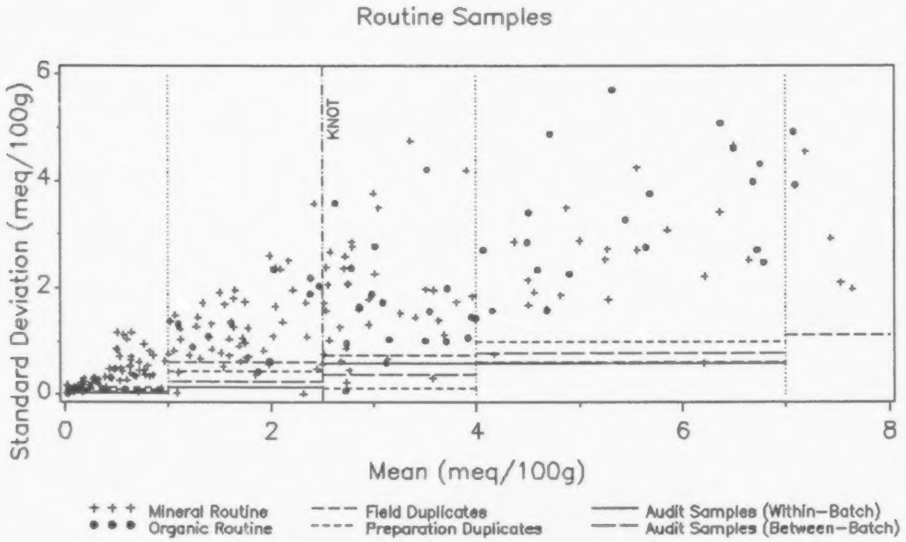


Figure 3-37. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for AL_KCL.



Note: Two mineral, three organic sampling class/horizon groups exceed plot boundaries.

Figure 3-38. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for AL_KCL.

Extractable Cations in Calcium Chloride

Of the six extractable cations in calcium chloride, the analytical within-batch precision DQOs were satisfied only for AL_CL2, although CA_CL2 only slightly exceeded the DQO (see Table 3-7). The standard error for MG_CL2 was more than three times higher than the DQO. These cations did not meet the DQOs possibly because the percent RSD was applied across the total concentration range whereas the other chemical parameter group had a two-tier DQO which, at the low concentration, which was expressed as a standard deviation.

The audit sample concentrations for this group of parameters were very low and this resulted in high RSDs. It appears that a two-tiered DQO should have been defined for this parameter group.

There was a general trend of increasing standard deviation with increased sources of confounded error. For the QA samples overall, CA_CL2 had the highest precision and K_CL2 had the lowest precision.

Figures 3-39 through 3-50 are plots of audit sample data in relation to the DQOs and of the routine sample data in relation to the QA samples. Supplemental information relating to the delta and proportion values is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-7. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of the Extractable Cations in Calcium Chloride

Data set[a]	Parameter	df[b]	RSD[c] %	DQO[c] %	Pairs>DQO	
					n	%
AS	CA_CL2	50	5.3	5	15	30.0
	MG_CL2	49	35.4	10	24	49.0
	K_CL2	50	12.5	10	15	30.0
	NA_CL2	50	12.4	10	22	44.0
	FE_CL2	40	14.9	10	16	40.0
	AL_CL2	59	8.5	10	19	32.2
PD	CA_CL2	55	6.4		13	23.6
	MG_CL2	54	30.6		23	42.6
	K_CL2	55	203.0		27	49.1
	NA_CL2	55	35.5		26	47.3
	FE_CL2	33	26.1		23	69.7
	AL_CL2	51	15.0		30	58.8
FD	CA_CL2	240	5.5		73	30.4
	MG_CL2	239	46.1		91	38.0
	K_CL2	240	100.6		125	52.0
	NA_CL2	240	33.4		143	59.5
	FE_CL2	161	68.1		89	55.3
	AL_CL2	247	27.4		147	59.4
S/H	CA_CL2	1076	27.1			
	MG_CL2	1075	85.3			
	K_CL2	1076	124.7			
	NA_CL2	1076	156.0			
	FE_CL2	838	235.9			
	AL_CL2	1075	92.5			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Relative standard deviations data for mineral soil samples, expressed in percent.

CA_CL2

Extractable Calcium in Calcium Chloride

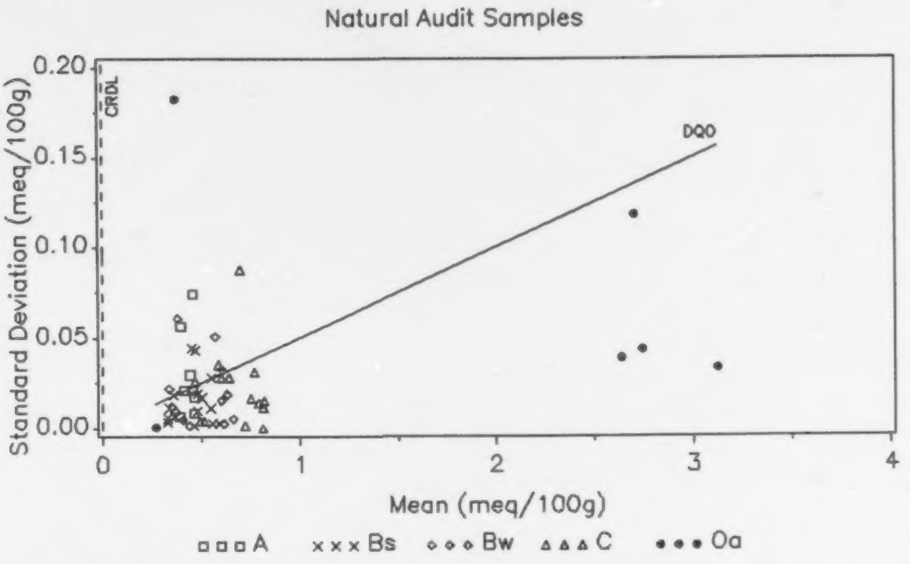
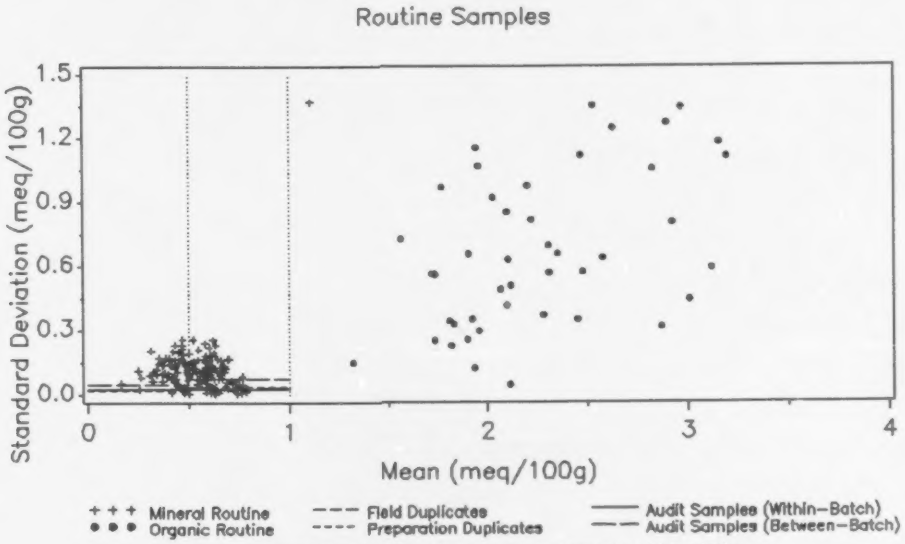


Figure 3-39. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for CA_CL2.

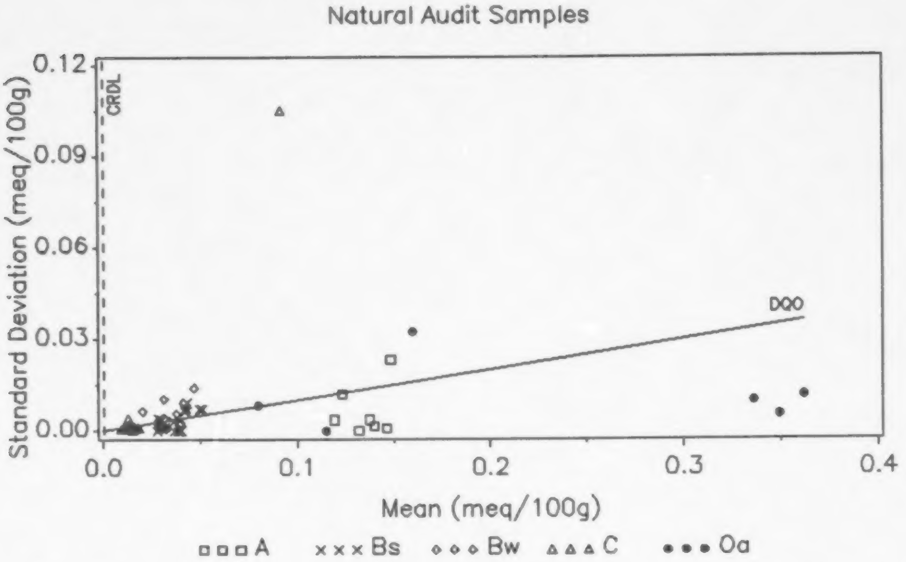


Note: Six organic sampling class/horizon groups exceed plot boundaries.

Figure 3-40. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for CA_CL2.

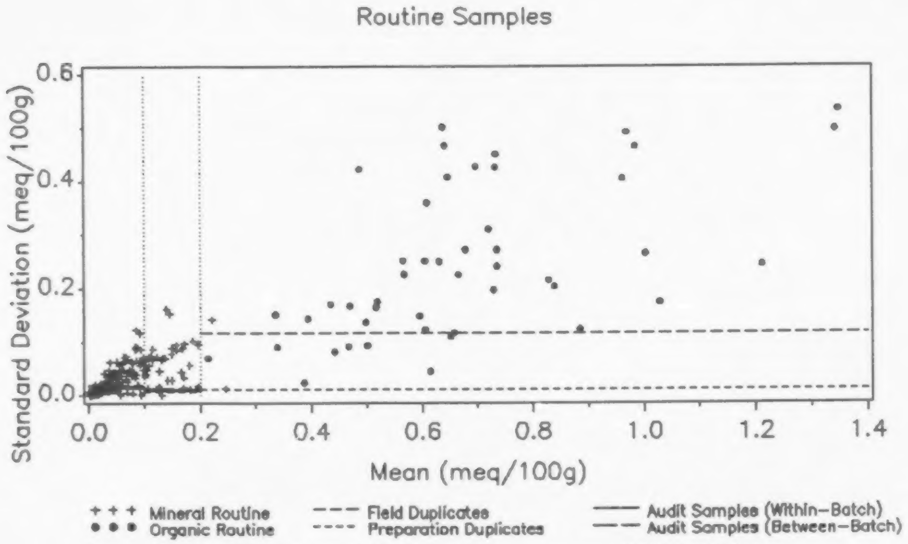
MG_CL2

Extractable Magnesium in Calcium Chloride



Natural Audit Samples

Figure 3-41. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for MG_CL2.



Routine Samples

Note: Three organic sampling class/horizon groups exceed plot boundaries.

Figure 3-42. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for MG_CL2.

K_CL2

Extractable Potassium in Calcium Chloride

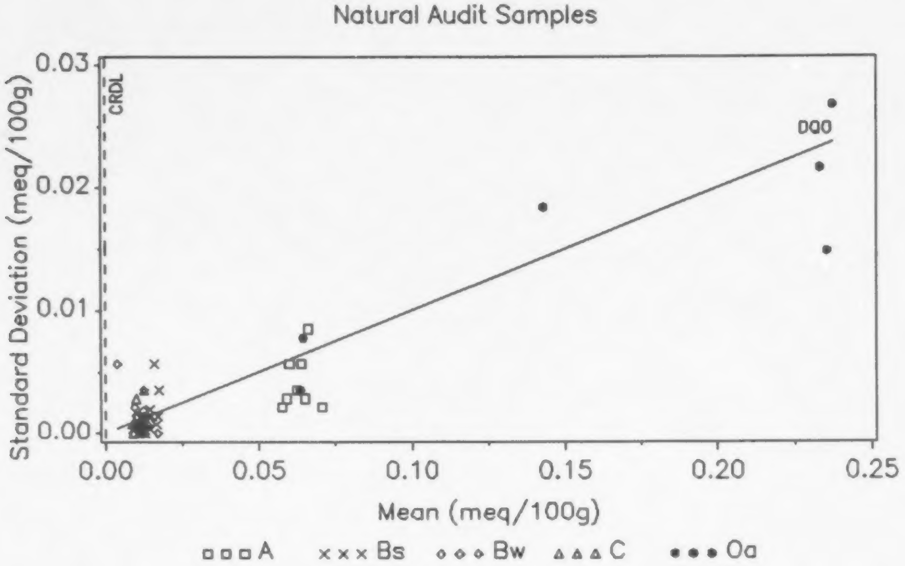
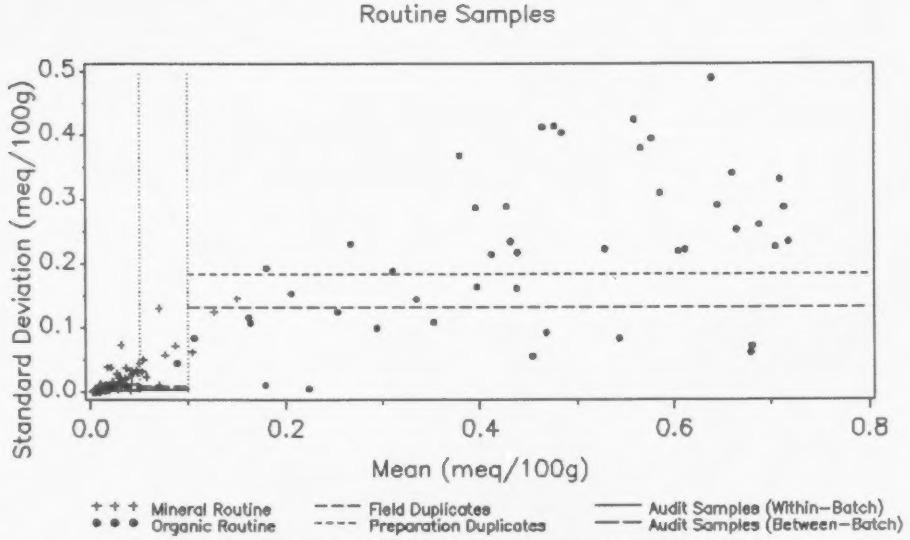


Figure 3-43. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for K_CL2.



Note: Four organic sampling class/horizon groups exceed plot boundaries.

Figure 3-44. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for K_CL2.

NA_CL2

Extractable Sodium in Calcium Chloride

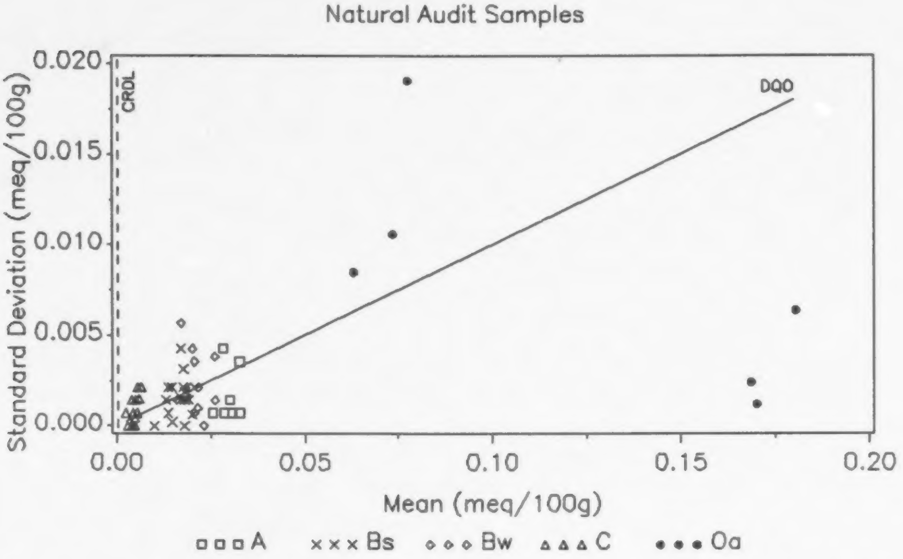
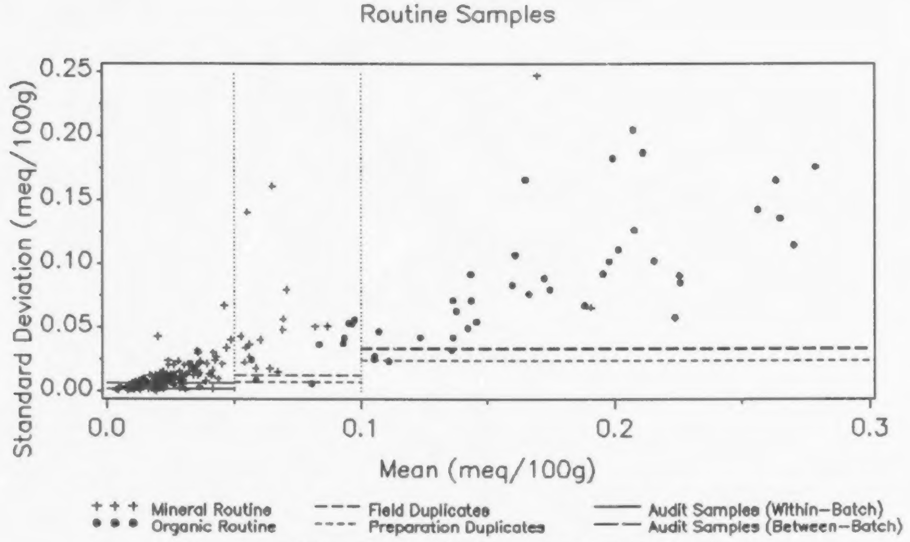

Natural Audit Samples

Figure 3-45. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for NA_CL2.


Routine Samples

Note: Four organic sampling class/horizon groups exceed plot boundaries.

Figure 3-46. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for NA_CL2.

FE_CL2

Extractable Iron in Calcium Chloride

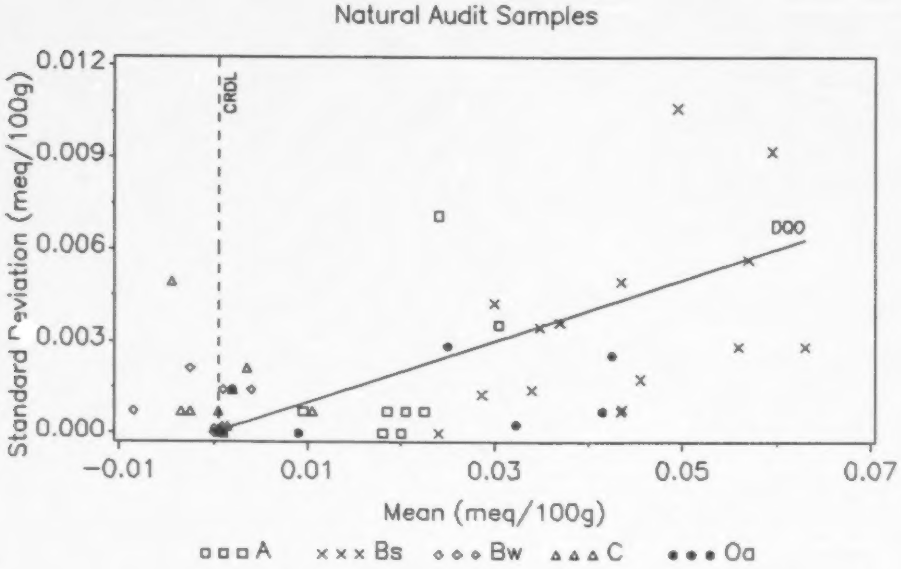
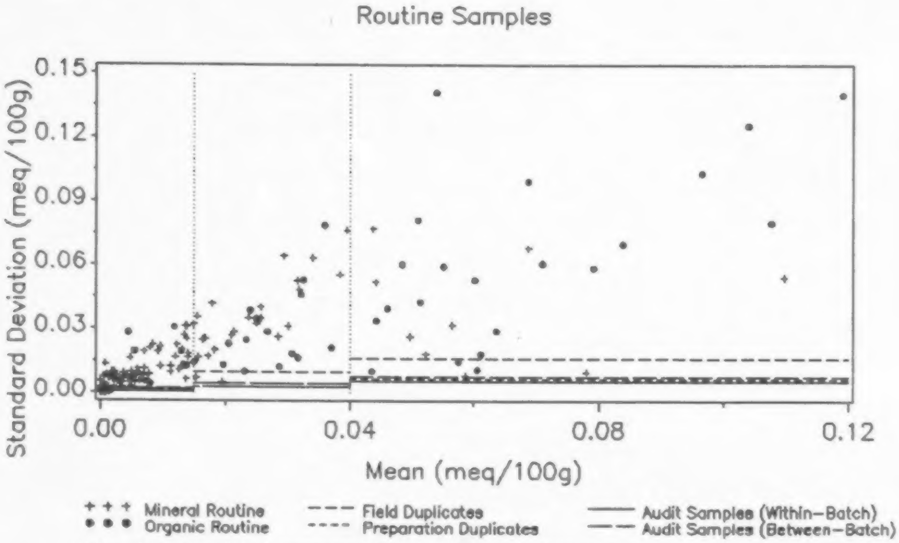


Figure 3-47. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for FE_CL2.



Note: Fourteen mineral, seven organic sampling class/horizon groups exceed plot boundaries.

Figure 3-48. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for FE_CL2.

AL_CL2

Extractable Aluminum in Calcium Chloride

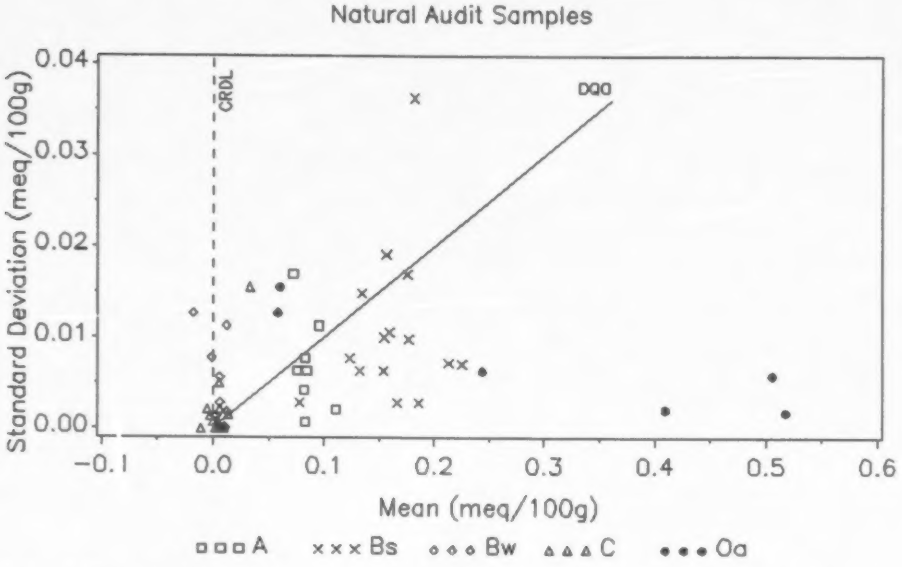
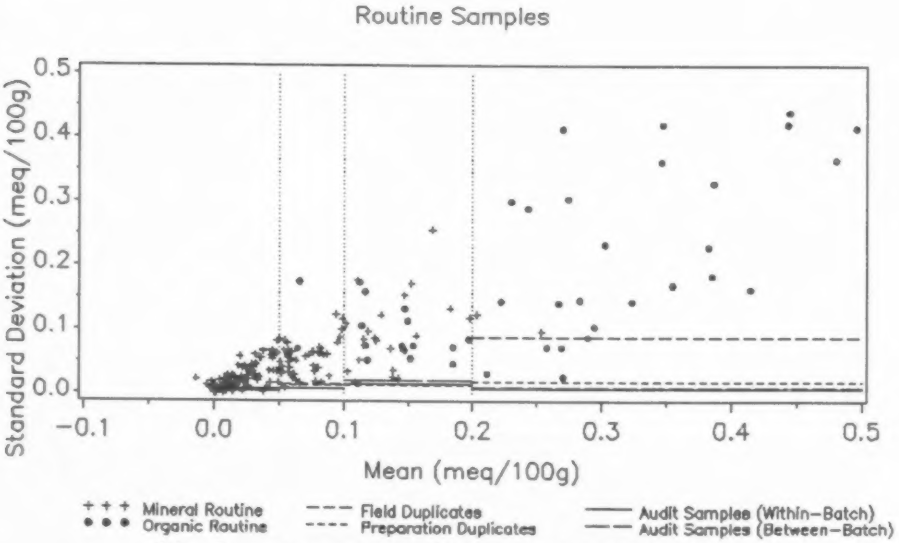


Figure 3-49. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for AL_CL2.



Note: Five organic sampling class/horizon groups exceed plot boundaries.

Figure 3-50. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for AL_CL2.

Extractable Iron and Aluminum

The analytical within-batch precision DQOs for the extractable iron and aluminum parameters were satisfied except for FE_AO below the knot (see Table 3-8). In this case, the standard error exceeded the DQO only slightly because of one inordinate audit pair. A general pattern of increasing standard deviation with increased sources of confounded error was maintained both below and above the knot.

For the QA samples below the knot, FE_PYP had the highest precision and FE_AO had the lowest precision overall. Above the knot, AL_PYP had the highest precision and AL_AO had the lowest precision.

Figures 3-51 through 3-62 are plots of the audit sample data in relation to the DQOs and of the routine sample data in relation to the QA samples. Supplemental information relating to the delta and proportion values is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-8. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of Extractable Iron and Aluminum

Data set[a]	Parameter	Below the knot[c]					Above the knot[c]				
		df[b]	SD wt %	DQO wt %	Pairs>DQO n	Pairs>DQO %	df	RSD %	DQO %	Pairs>DQO n	Pairs>DQO %
AS	FE_PYP	14	0.0075	0.05	0	0.0	36	7.3	15	1	2.8
	AL_PYP	14	0.0100	0.05	0	0.0	36	7.9	15	2	5.6
	FE_AO	14	0.0600	0.05	1	7.1	36	10.6	15	4	11.1
	AL_AO	14	0.0133	0.05	0	0.0	36	8.2	15	3	8.3
	FE_CD	14	0.0165	0.05	0	0.0	36	5.4	15	1	2.8
	AL_CD	16	0.0073	0.05	0	0.0	34	6.8	15	2	5.9
PD	FE_PYP	47	0.0143		0	0.0	7	26.9		1	14.3
	AL_PYP	45	0.0235		4	8.9	10	6.6		0	0.0
	FE_AO	41	0.0405		3	7.3	14	10.6		3	21.4
	AL_AO	35	0.0221		1	2.9	20	16.5		6	30.0
	FE_CD	20	0.0081		0	0.0	35	10.2		4	11.4
	AL_CD	46	0.0136		0	0.0	9	15.1		2	22.2
FD	FE_PYP	144	0.0300		6	4.2	96	17.1		19	19.8
	AL_PYP	131	0.0467		11	8.4	110	11.8		13	11.8
	FE_AO	107	0.0434		10	9.3	134	17.4		26	19.4
	AL_AO	102	0.0223		6	5.9	139	75.9		27	19.4
	FE_CD	55	0.0548		4	7.3	185	15.4		30	16.2
	AL_CD	135	0.0430		8	5.9	105	13.5		15	14.3
S/H	FE_PYP	747	0.1323				329	95.3			
	AL_PYP	690	0.1183				386	53.4			
	FE_AO	555	0.1515				522	88.1			
	AL_AO	484	0.1165				593	84.0			
	FE_CD	294	0.1737				781	66.2			
	AL_CD	689	0.1418				386	66.5			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in reporting units and percent, respectively, for mineral soil samples below and above the knot point of 0.33 weight percent.

FE_PYP

Extractable Iron in Sodium Pyrophosphate

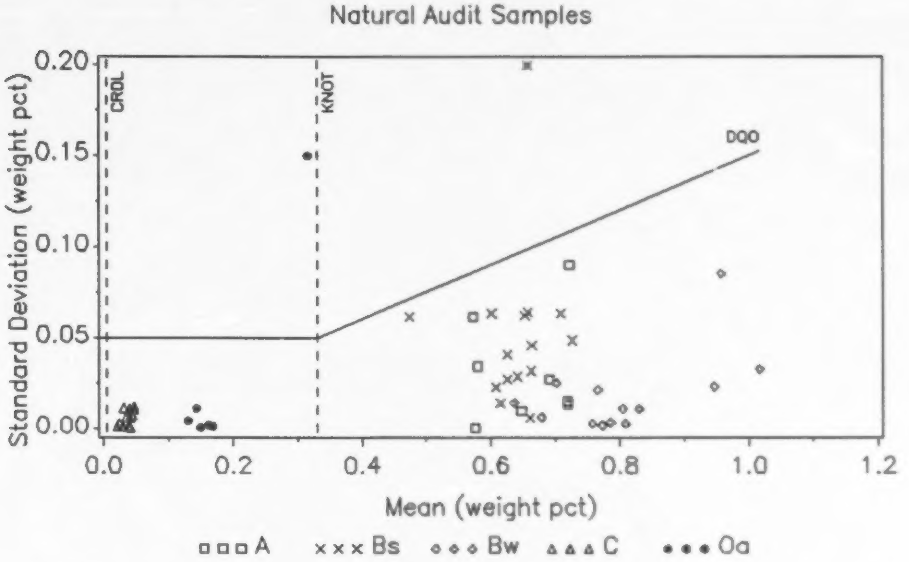
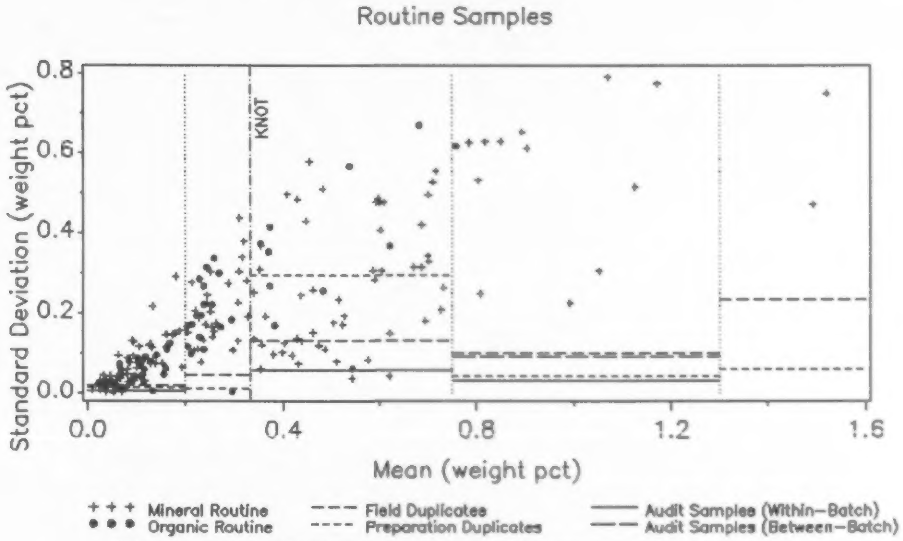


Figure 3-51. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for FE_PYP.



Note: Ten mineral, one organic sampling class/horizon groups exceed plot boundaries.

Figure 3-52. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for FE_PYP.

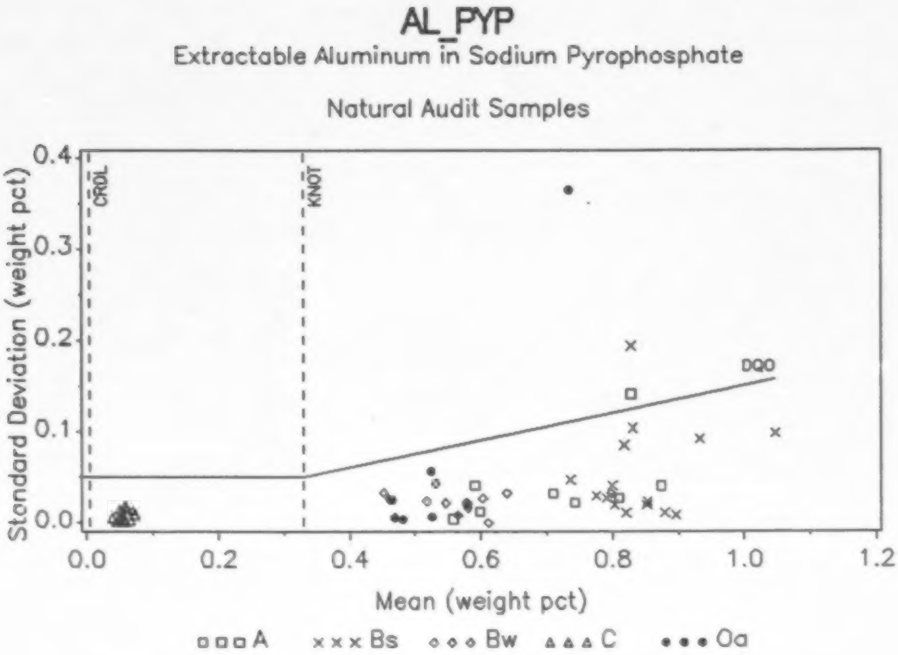
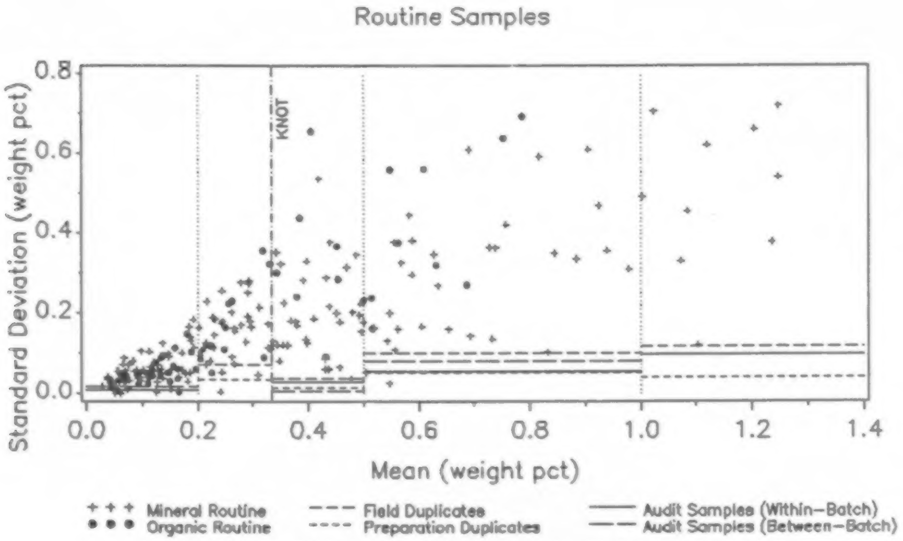


Figure 3-53. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for AL_PYP.



Note: Three mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-54. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for AL_PYP.

FE_AO

Extractable Iron in Acid Oxalate

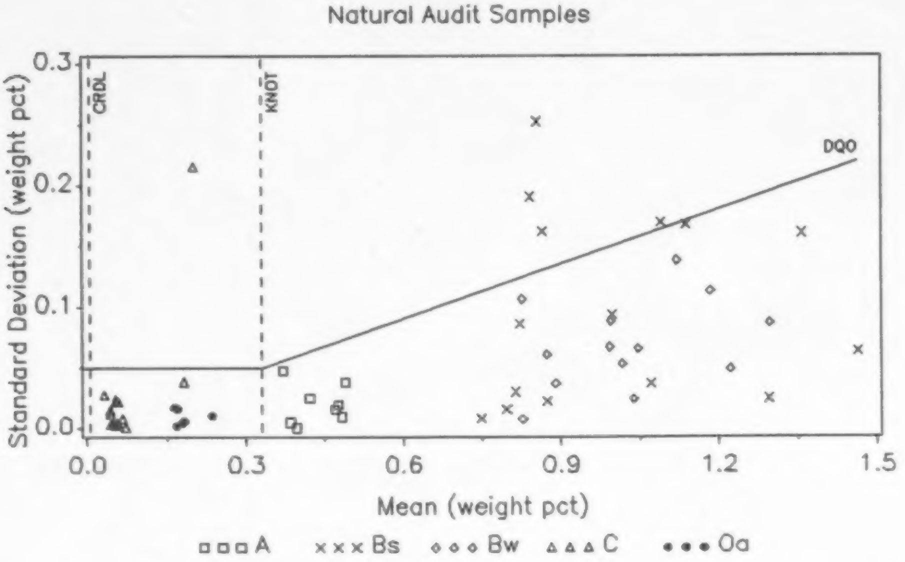
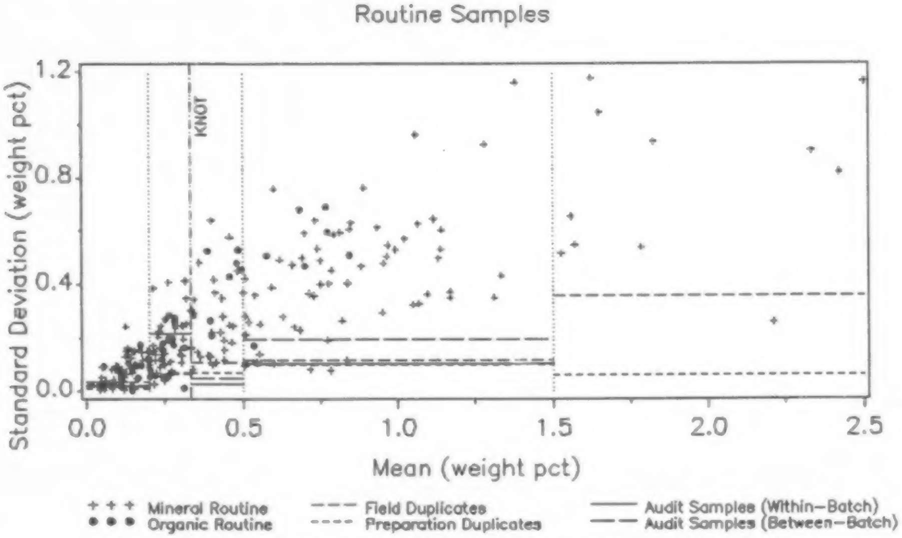


Figure 3-55. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for FE_AO.



Note: Two mineral, one organic sampling class/horizon groups exceed plot boundaries.

Figure 3-56. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for FE_AO.

AL_AO

Extractable Aluminum in Acid Oxalate

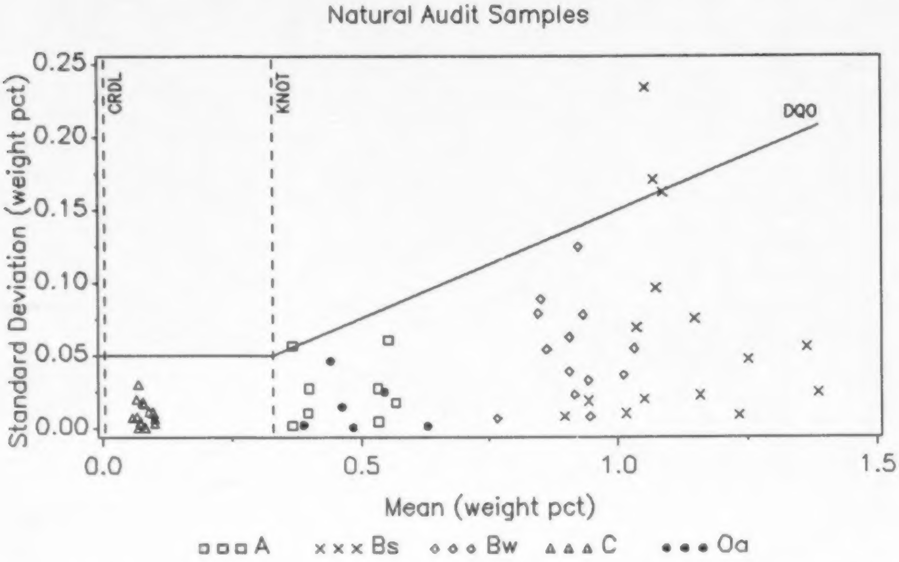
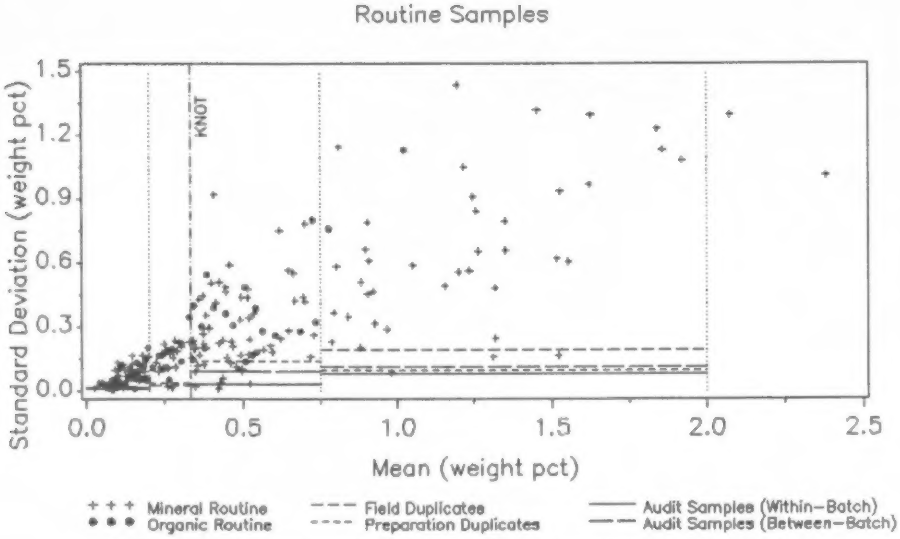


Figure 3-57. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for AL_AO.



Note: Four mineral, one organic sampling class/horizon groups exceed plot boundaries.

Figure 3-58. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for AL_AO.

FE_CD

Extractable Iron in Citrate Dithionite

Natural Audit Samples

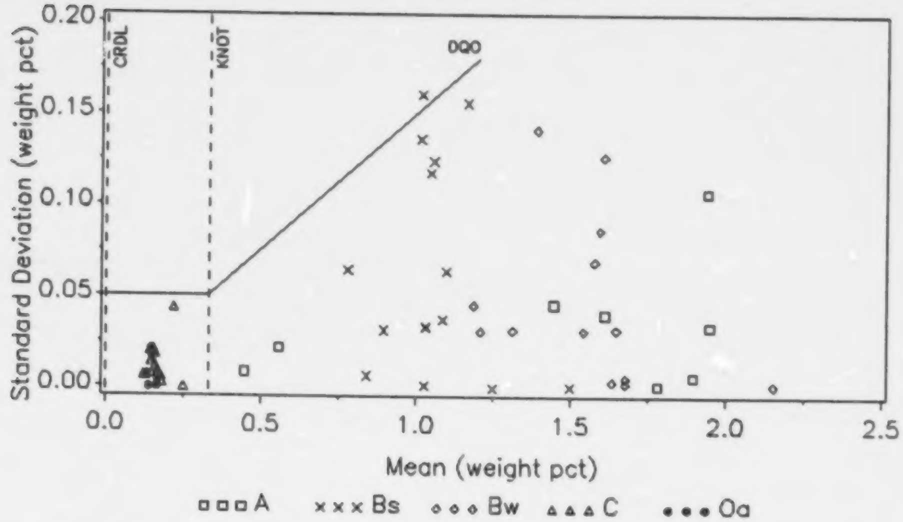
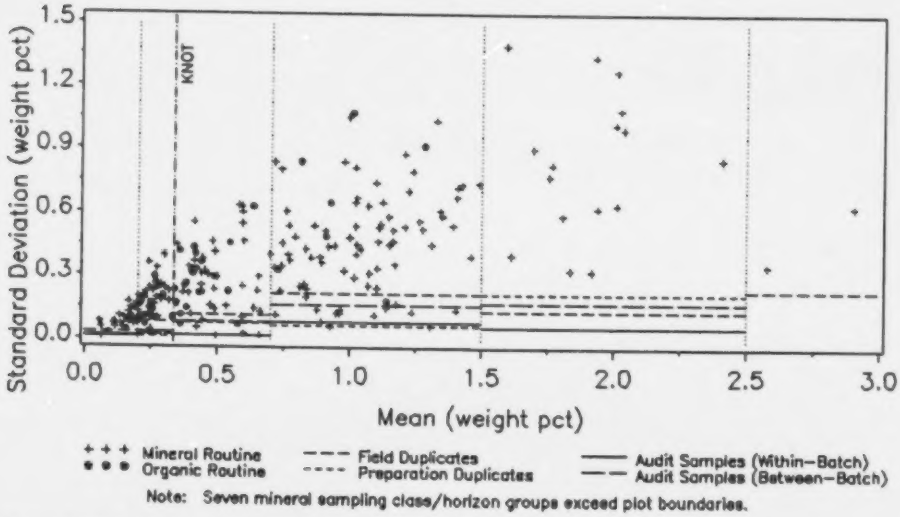


Figure 3-59. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for FE_CD.

Routine Samples



Note: Seven mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-60. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for FE_CD.

AL_CD

Extractable Aluminum in Citrate Dithionite

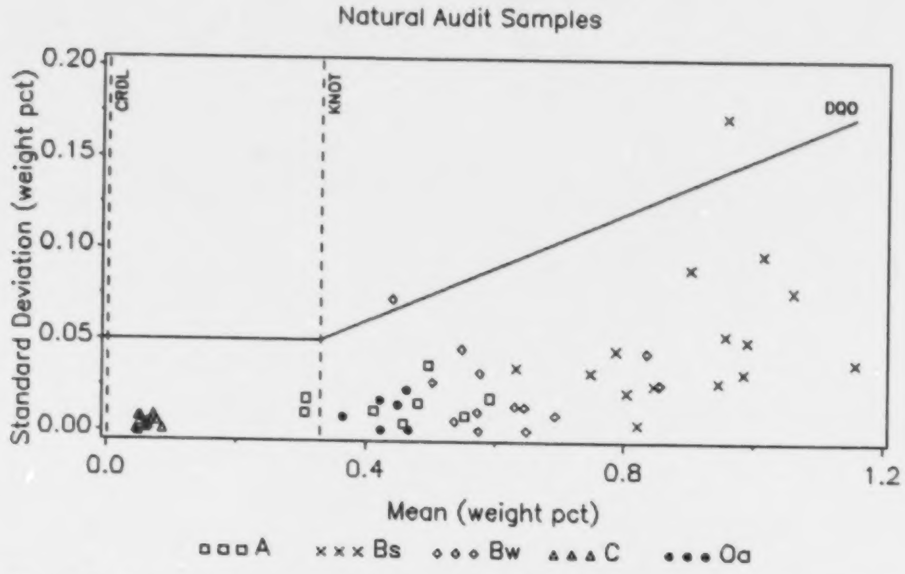
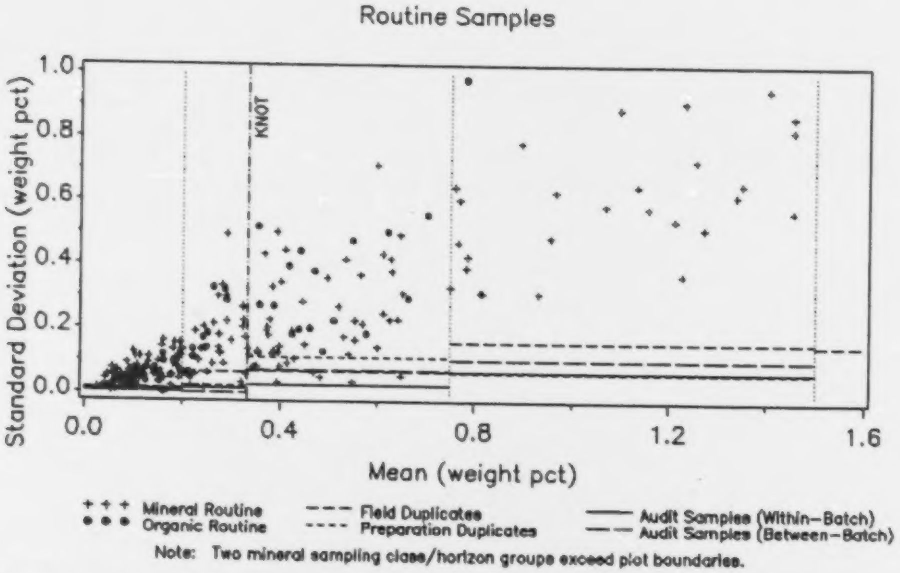


Figure 3-61. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for AL_CD.



Note: Two mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-62. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for AL_CD.

Extractable Sulfate and Sulfate Adsorption Isotherms

The analytical within-batch precision DQOs for the sulfate parameters were satisfied except for SO4_0, where the standard error only slightly exceeded the DQO both below and above the knot. In both cases, the number of pairs exceeding the DQO was approximately 50 percent.

There was a general trend of increasing standard deviation with increased sources of confounded error for the extractable sulfate parameters below the knot. However, this was not the case above the knot for SO4_H20, where the preparation error was 10 times higher than the analytical error and also higher than the field sampling error.

Figures 3-63 through 3-78 are plots of the audit sample data in relation to the DQOs and of the routine sample data in relation to the QA samples. Supplemental information relating to the delta and proportion values is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-9. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of Extractable Sulfate and Sulfate Adsorption Isotherms

Data set[a]	Parameter	Below the knot[c]					Above the knot[c]				
		df[b]	SD	DQO	Pairs>DQO		df	RSD	DQO	Pairs>DQO	
			— units —		n	%		%	%	n	%
AS	SO4_H2O	25	0.7194	1.00	2	7.8	24	6.9	10	5	20.8
	SO4_PO4	14	0.5110	1.00	1	7.1	36	7.3	10	5	13.9
	SO4_0	14	0.0760	0.05	8	57.1	36	6.0	5	17	47.2
	SO4_2	•	•	0.05	•	•	50	3.4	5	6	12.0
	SO4_4	•	•	0.05	•	•	50	4.0	5	8	16.0
	SO4_8	•	•	0.05	•	•	50	3.2	5	2	4.0
	SO4_16	•	•	0.05	•	•	50	3.8	5	5	10.0
	SO4_32	•	•	0.05	•	•	50	2.9	5	6	12.0
PD	SO4_H2O	45	1.3897		7	15.6	10	62.6		5	50.0
	SO4_PO4	28	0.7404		5	17.5	26	20.3		7	26.9
	SO4_0	42	0.0782		8	19.0	13	11.1		5	38.5
	SO4_2	•	•		•	•	55	9.0		11	20.0
	SO4_4	•	•		•	•	55	5.8		9	16.4
	SO4_8	•	•		•	•	55	3.5		6	10.9
	SO4_16	•	•		•	•	55	3.0		6	10.9
	SO4_32	•	•		•	•	55	5.5		6	10.9
FD	SO4_H2O	136	0.9462		26	19.1	105	40.4		26	24.8
	SO4_PO4	66	1.3653		20	30.3	172	20.9		49	28.5
	SO4_0	132	0.0920		50	37.9	109	17.6		46	42.2
	SO4_2	4	0.0485		2	50.0	237	6.7		69	29.1
	SO4_4	•	•		•	•	241	15.7		50	20.7
	SO4_8	•	•		•	•	241	4.0		35	14.5
	SO4_16	•	•		•	•	241	4.5		39	16.2
	SO4_32	•	•		•	•	241	3.6		25	10.4
S/H	SO4_H2O	728	4.1391				349	71.8			
	SO4_PO4	248	6.7118				826	149.4			
	SO4_0	680	0.2990				396	73.1			
	SO4_2	•	•				1076	34.8			
	SO4_4	•	•				1076	24.9			
	SO4_8	•	•				1076	17.6			
	SO4_16	•	•				1077	13.9			
	SO4_32	•	•				1077	10.7			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in reporting units and percent, respectively, for mineral soil samples below and above the knot point of 10.0 mg S/kg for extractable sulfate and 1.0 mg S/L for the sulfate isotherms (SO4_0 to SO4_32); a dot signifies a lack of data occupying that range.

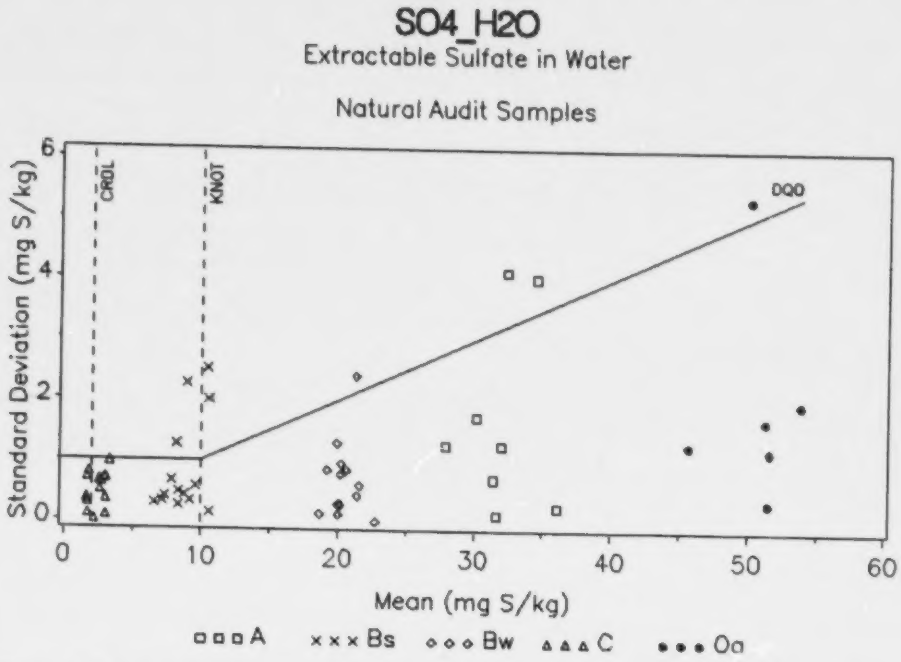
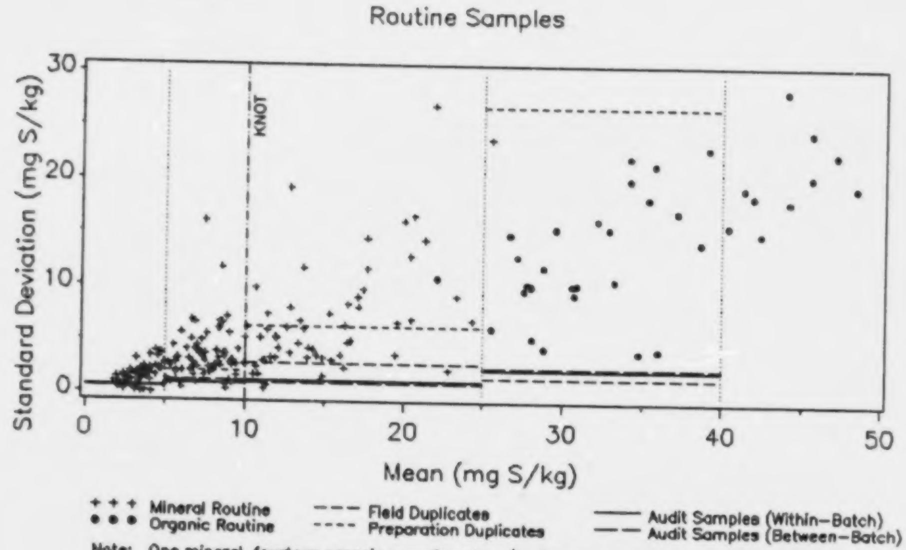


Figure 3-63. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SO4_H2O.



Note: One mineral, fourteen organic sampling class/horizon groups exceed plot boundaries.

Figure 3-64. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SO4_H2O.

SO4_PO4

Extractable Sulfate in Sodium Phosphate

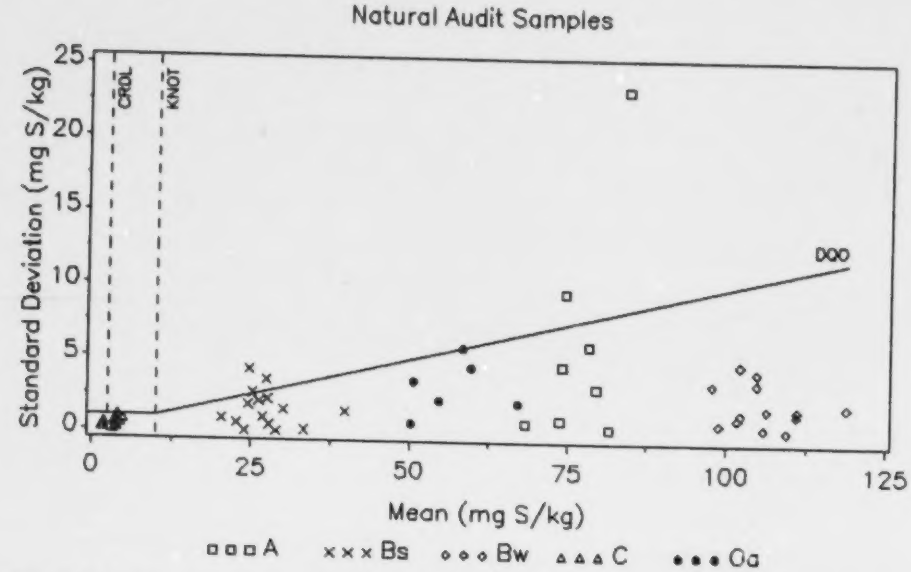
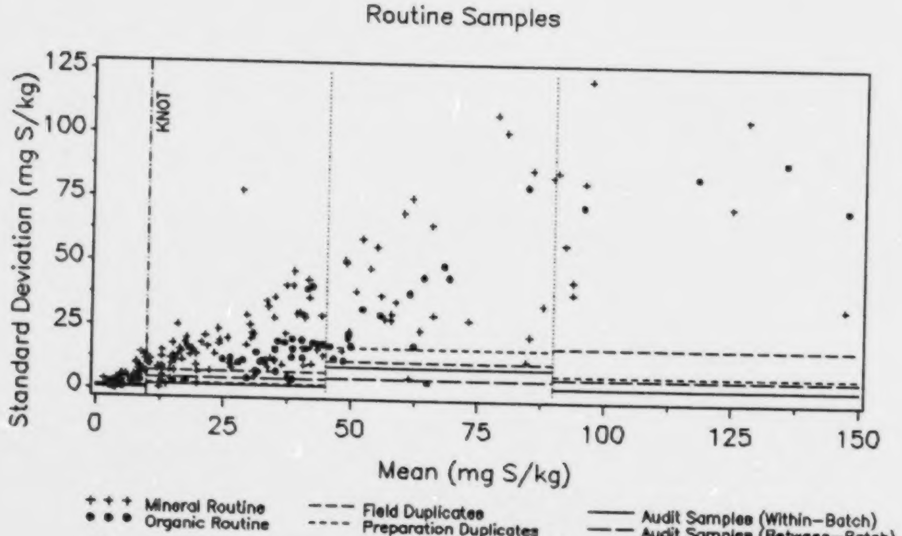


Figure 3-65. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SO4_PO4.



Note: Seven mineral, three organic sampling class/horizon groups exceed plot boundaries.

Figure 3-66. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SO4-_PO4.

SO4_0

0 mg S/L Sulfate Isotherm

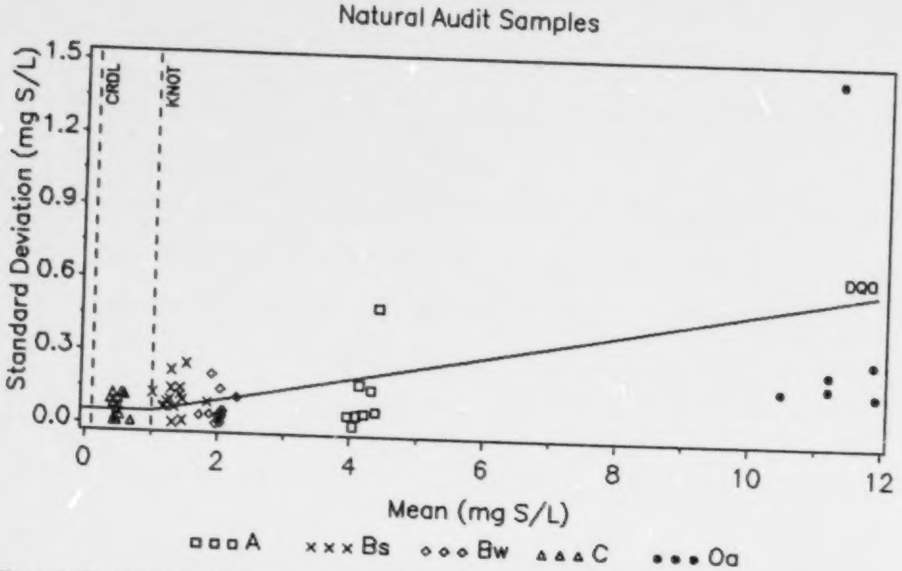
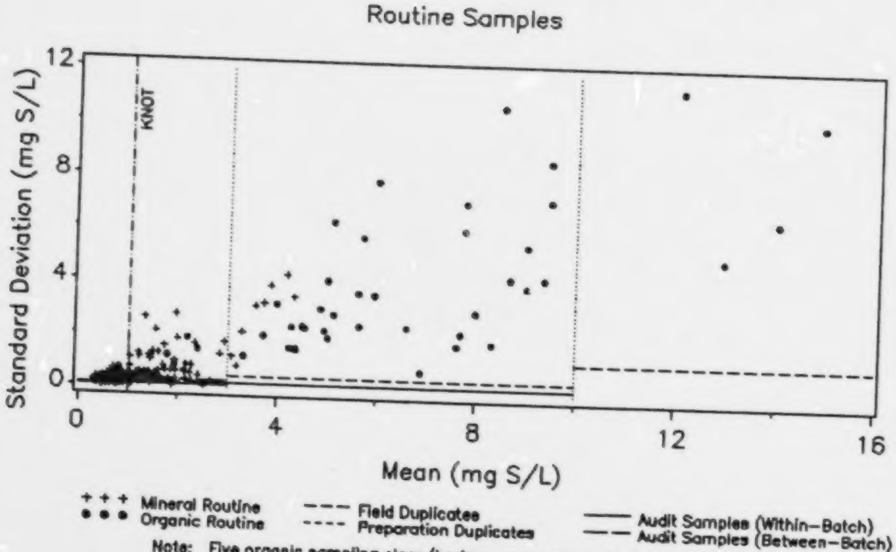
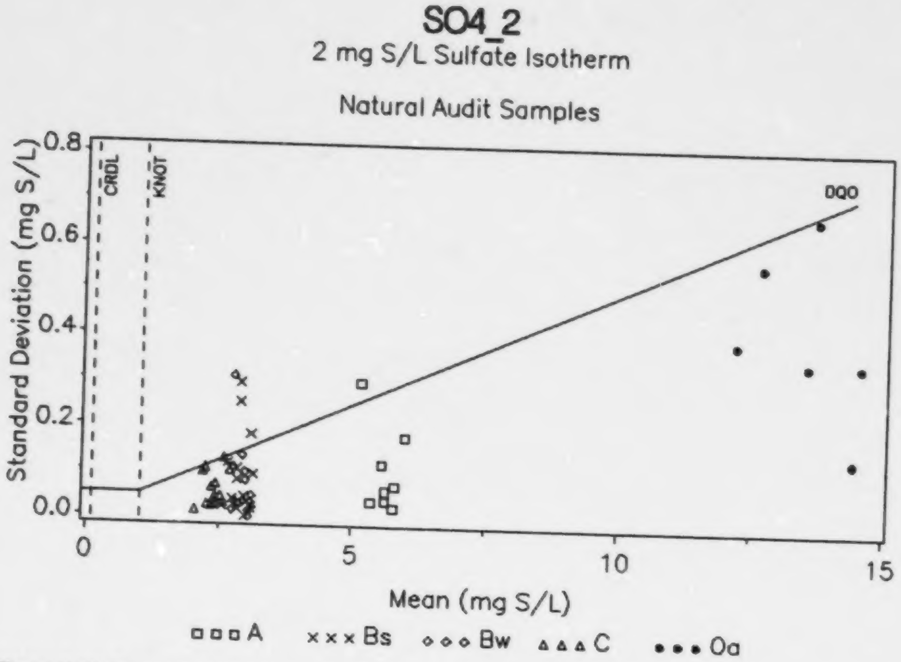


Figure 3-67. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SO4_0.



Note: Five organic sampling class/horizon groups exceed plot boundaries.

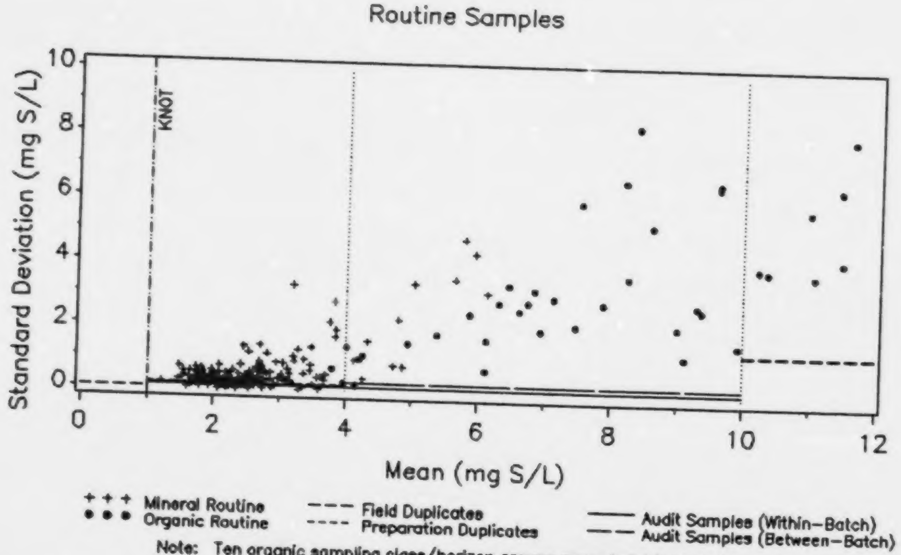
Figure 3-68. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SO4_0.


SO4_2

2 mg S/L Sulfate Isotherm

Natural Audit Samples

Figure 3-69. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SO4_2.


Routine Samples

Note: Ten organic sampling class/horizon groups exceed plot boundaries.

Figure 3-70. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SO4_2.

SO4_4

4 mg S/L Sulfate Isotherm

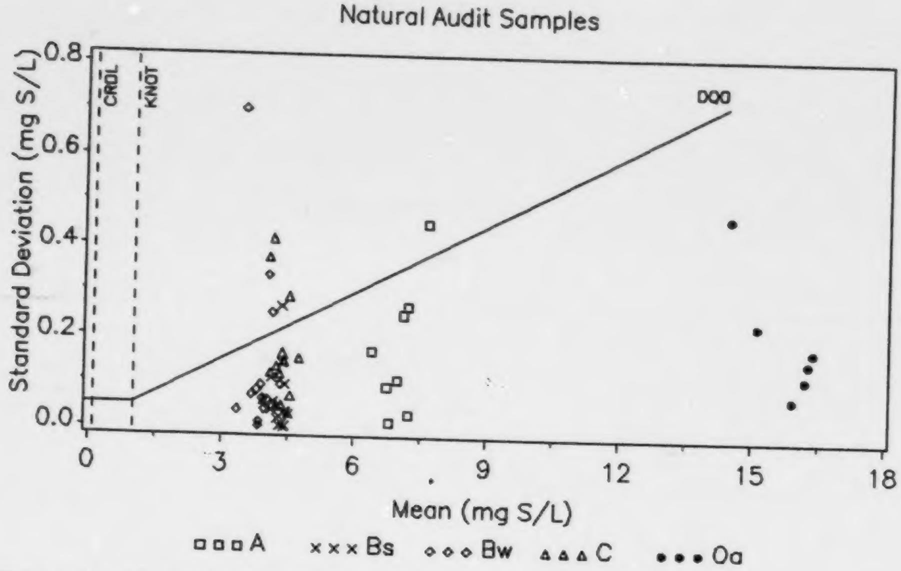


Figure 3-71. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SO4_4.

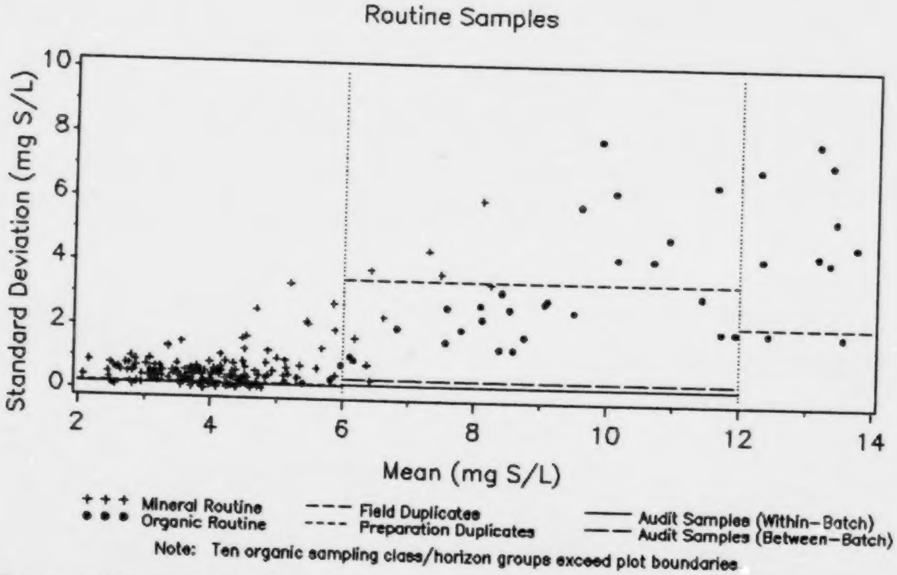


Figure 3-72. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SO4_4.

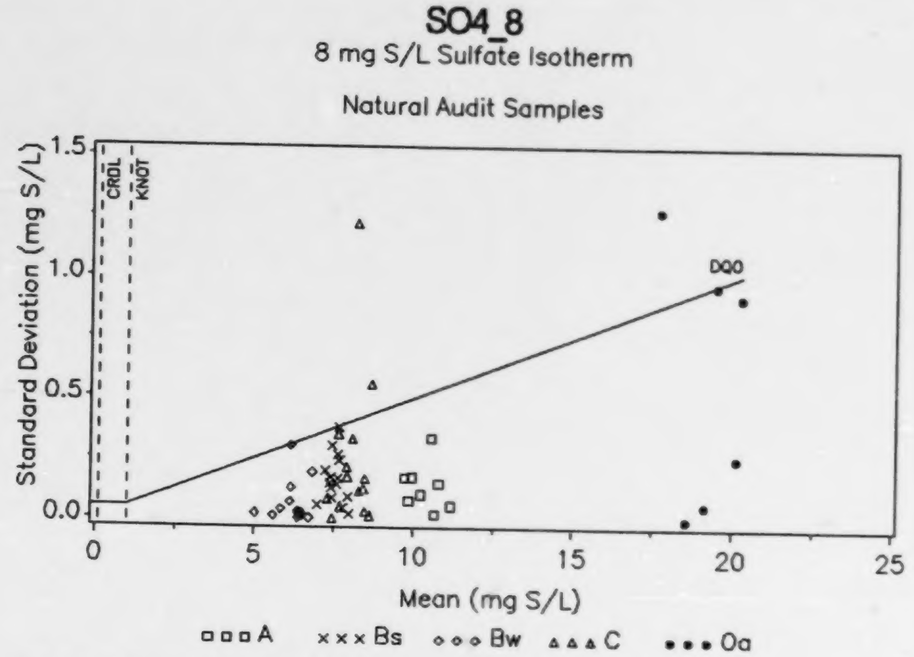
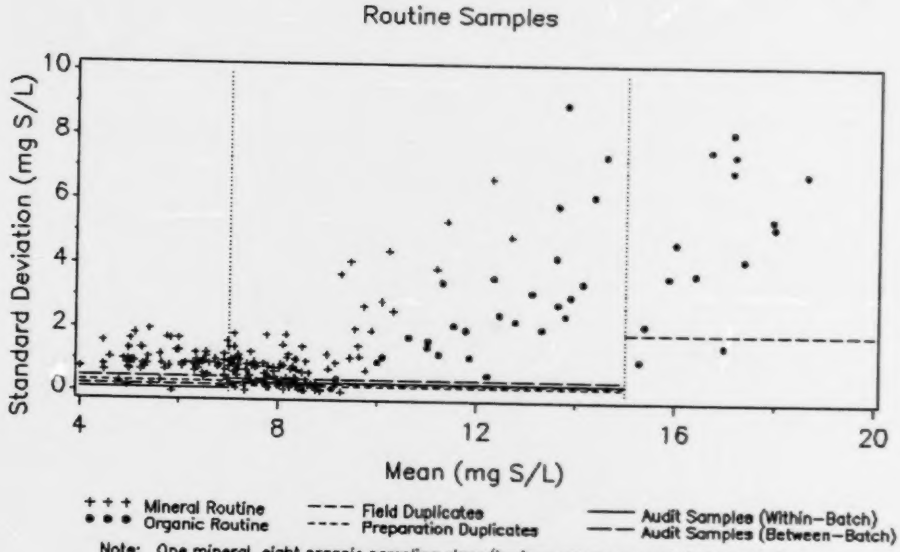


Figure 3-73. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SO4_8.



Note: One mineral, eight organic sampling class/horizon groups exceed plot boundaries.

Figure 3-74. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SO4_8.

SO4_16

16 mg S/L Sulfate Isotherm

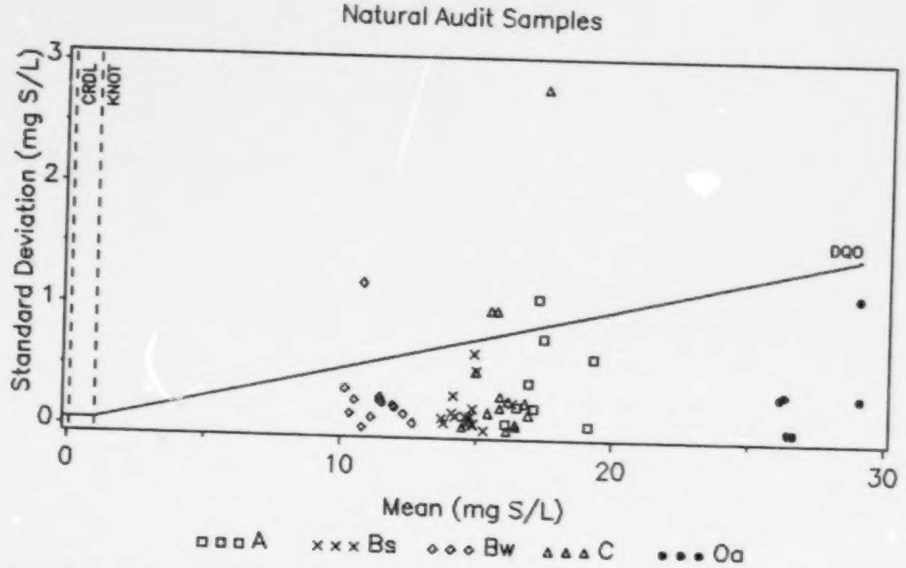
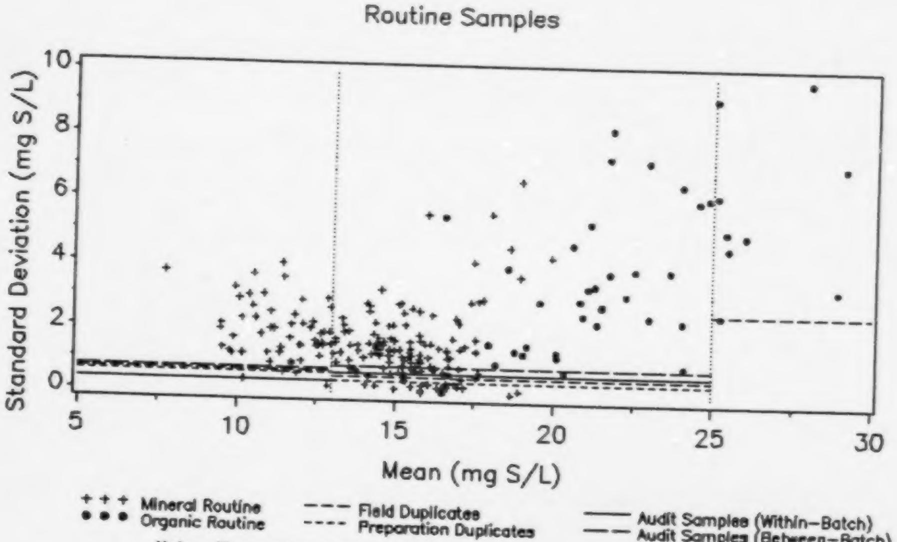

Natural Audit Samples

Figure 3-75. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SO4_16.


Routine Samples

Note: Six organic sampling class/horizon groups exceed plot boundaries.

Figure 3-76. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SO4_16.

SO4_32

32 mg S/L Sulfate Isotherm

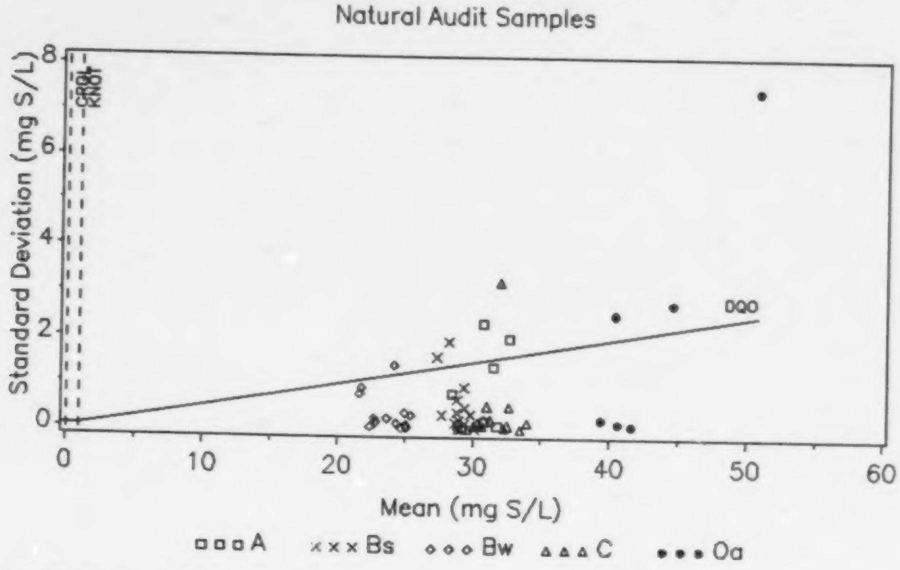
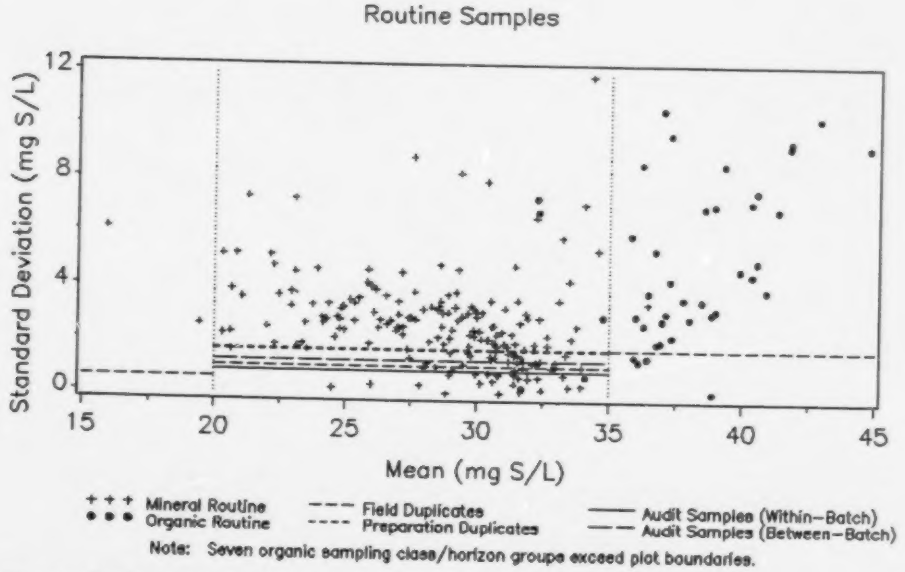


Figure 3-77. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for SO4_32.



Note: Seven organic sampling class/horizon groups exceed plot boundaries.

Figure 3-78. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SO4_32.

Total Carbon, Nitrogen, and Sulfur

The analytical within-batch precision DQOs were satisfied for total carbon, nitrogen, and sulfur except for N_TOT above the knot (see Table 3-10). For S_TOT, there were no audit sample data above the knot and it was not possible to examine precision in this tier. A general pattern of increasing standard deviation with increased sources of confounded error was maintained below, but not above the knot, where preparation error was high. For the QA samples below the knot, S_TOT had the highest precision overall and C_TOT had the lowest precision overall.

Figures 3-79 through 3-84 are plots of audit sample data in relation to the DQOs and routine sample data in relation to the QA samples. Supplemental information relating to the delta and proportion values is presented in Appendix C and the identification of inordinate values is presented in Appendix D.

Table 3-10. Achievement of Data Quality Objectives for Analytical Within-Batch Precision of Total Carbon, Nitrogen, and Sulfur

		Below the knot[c]					Above the knot[c]				
Data set[a]	Parameter	df[b]	SD wt%	DQO wt %	Pairs>DQO n	Pairs>DQO %	df	RSD %	DQO %	Pairs>DQO n	Pairs>DQO %
AS	C_TOT	14	0.0224	0.05	1	7.1	36	8.2	15	4	11.1
	N_TOT	10	0.0033	0.01	0	0.0	35	17.3	10	15	42.9
	S_TOT	45	0.0057	0.01	4	8.9	•	•	10	•	•
PD	C_TOT	28	0.0244		3	10.7	27	16.0		5	18.5
	N_TOT	42	0.0172		9	21.4	5	119.7		1	20.0
	S_TOT	44	0.0053		2	4.5	•	•		•	•
FD	C_TOT	50	0.0419		3	6.0	191	40.0		27	14.1
	N_TOT	125	0.0155		28	22.4	108	45.0		38	35.2
	S_TOT	214	0.0061		9	4.2	3	49.0		1	33.3
S/H	C_TOT	258	0.1326				619	70.2			
	N_TOT	726	0.0440				316	52.5			
	S_TOT	1038	0.0162				5	132.2			

[a] AS = Audit samples; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in reporting units and percent, respectively, for mineral soil samples below and above the knot point of 0.33 weight percent for carbon and 0.10 weight percent for nitrogen and sulfur; a dot signifies a lack of data occupying that range.

C_TOT
Total Carbon

Natural Audit Samples

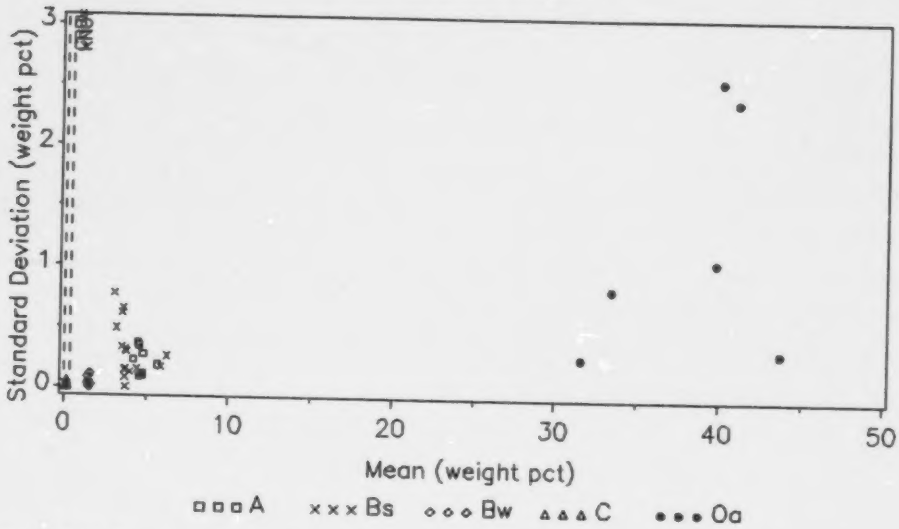
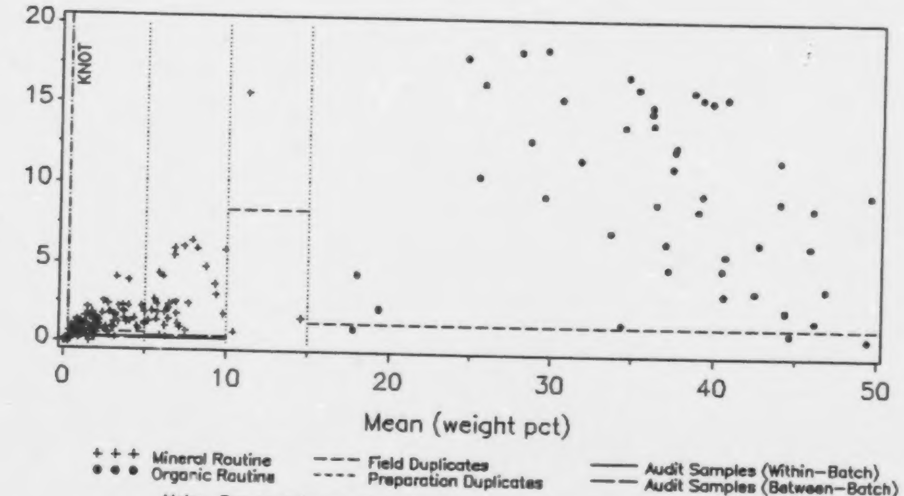


Figure 3-79. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for C_TOT.

Routine Samples



Note: Two organic sampling class/horizon groups exceed plot boundaries.

Figure 3-80. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for C_TOT.

N_TOT

Total Nitrogen

Natural Audit Samples

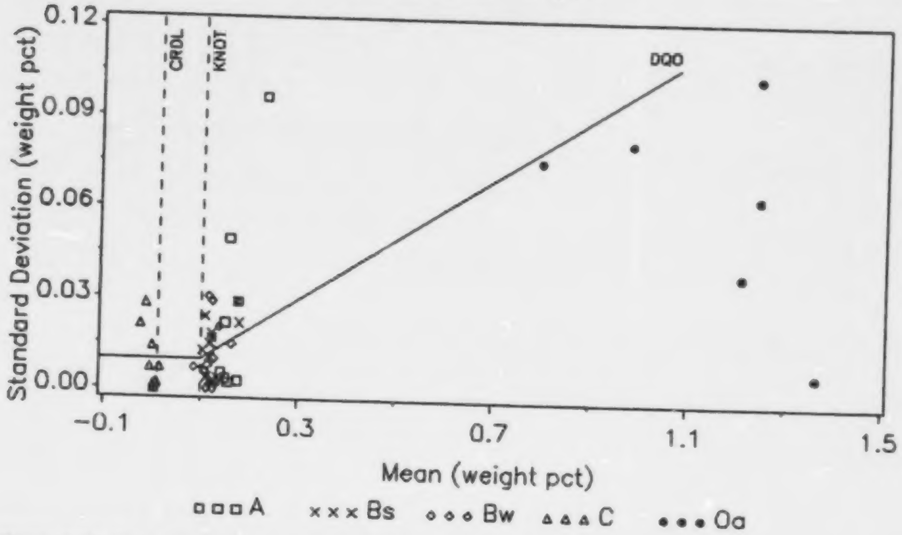
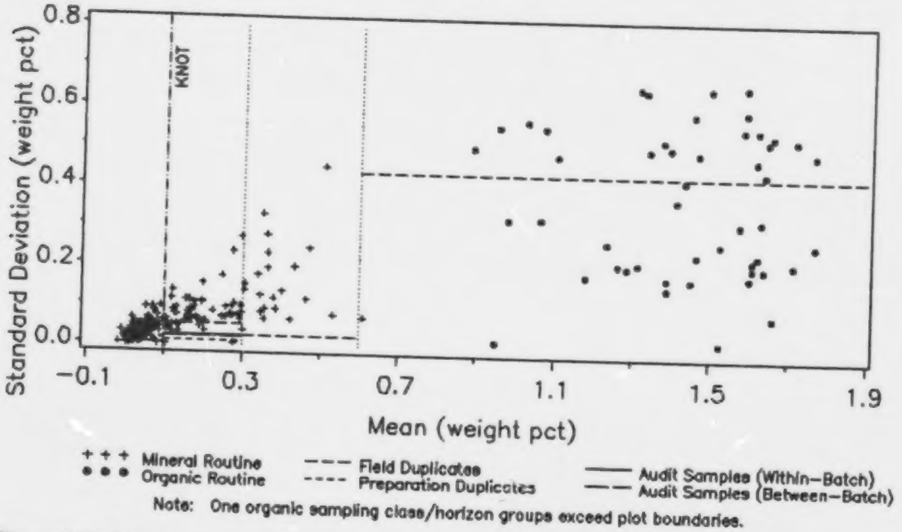


Figure 3-81. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for N_TOT.

Routine Samples



Note: One organic sampling class/horizon groups exceed plot boundaries.

Figure 3-82. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for N_TOT.

S_TOT

Total Sulfur

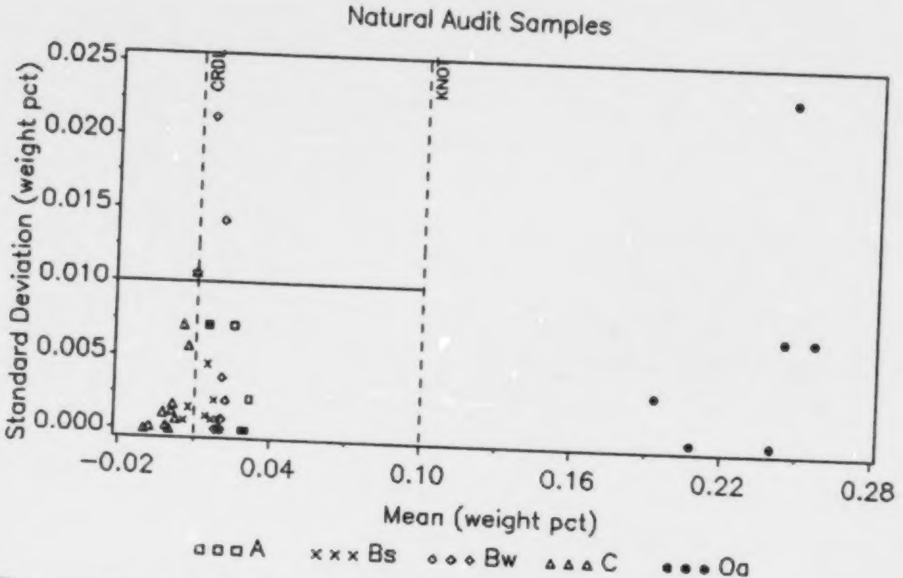
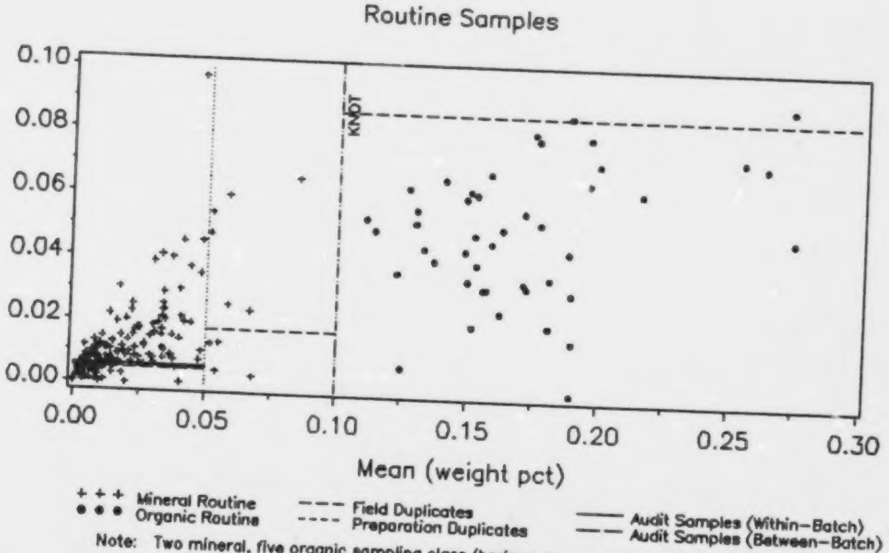


Figure 3-83. Range and frequency distribution of the natural audit samples and their relation to achievement of the analytical within-batch precision objective for S_TOT.



Note: Two mineral, five organic sampling class/horizon groups exceed plot boundaries.

Figure 3-84. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for S_TOT.

Within-Batch Precision

For each parameter, the standard deviations were pooled over the concentration range using the proportion (Pi) of routine data in the given windows to calculate delta values for within-batch and between-batch error (see Appendix C). Table 3-11 shows the delta values for within-batch estimates for field sampling, sample preparation, and analysis for the 51 parameters. The field sampling delta values contain the confounded error of sampling, preparation, and analysis. The sample preparation delta values contain the confounded error of preparation and analysis. The analytical delta values which were derived from the audit samples contain analytical laboratory error confounded with error due to audit sample preparation (which can be assumed to be negligible).

Within-batch precision estimates increased progressively, as expected, from analytical to sample preparation to field sampling. More specifically, Table 3-12 shows that these three precision components of the measurement error were estimated for six of the nine parameter groups. The data also indicate that the imprecision due to field sampling for the CEC parameters and the imprecision due to sample preparation for the soil pH group are negligible.

Between-Batch Precision

For the analytical component of data collection, it is assumed that each laboratory analyzed the soil samples on a batch-wise basis under conditions specific to each batch analysis, e.g., calibration curve and instrumentation settings. By ANOVA, the between-batch sum of squares was calculated for each parameter using the data from the audit samples. Table 3-11 shows the delta values for the between-batch precision estimates for the analytical component.

The cation exchange capacities, phosphate extractable sulfate and acidity in barium chloride-triethanolamine parameters generally showed the greatest variability when comparing analytical within and between-batch for the 51 parameters. These parameters could be considered as causing the greatest laboratory analytical difficulties from batch to batch. Several cases showed little difference between the within-batch and between-batch precision estimates. This shows good analytical repeatability by the laboratories from batch to batch using the prescribed methods. It could also indicate that the laboratories were extracting and analyzing across batches of samples, i.e., analyzing extracts from several batches at one time. This would reduce between-batch error. In several cases, the between-batch estimates were less than the within-batch estimates.

The expected between-batch analytical precision includes the expected within-batch analytical precision. If the ratio of between-batch precision to within-batch precision is less than one, there is no evidence of between-batch error. If the ratio is between 1 and 1.5, the observed error could be merely due to sample fluctuations. If the ratio is greater than 1.5, then the between-batch error is substantial and the magnitude of between-batch precision could be as large as 50 percent of the within-batch precision. See Table 3-12 for a summary of within-batch and between-batch precision estimates.

Accuracy (Interlaboratory Differences)

Significant Differences Among Laboratories

Table 3-13 shows the laboratories which exhibited significantly lower differences using Scheffe's pair-wise multiple comparison test for 40 of the 51 parameters which showed such differences. Data are presented for significant differences (.05 level) and for highly significant differences (.01 level) which are designated in the table by two asterisks. In many cases, the results of one laboratory are highly significantly different from those of the other three laboratories. The reader has several options to take when using these data for these specific cases. The user should exercise caution when interpreting the data. See Schmoyer et al. (In press) for additional details.

For the Oa audit sample, laboratory differences were highly significant for AL_KCL, CA_CL2, and AL_CL2. Significant differences were shown mainly for cations in 0.002M

Table 3-11. Within-Batch and Between-Batch Precision Estimates

		Within-batch			Between-batch
Parameter	Units	Field Sampling δ-values	Sample Preparation δ-values	Analytical δ-values	Analytical Standard Deviation
MOIST[a]	wt %	0.38	0.40	0.10	0.13
SP_SUR[a]	m^2/g	4.47	2.60	3.89	4.20
SAND[a]	wt %	2.26	2.28	1.13	1.46
VCOS[a]	"	1.20	1.09	1.18	0.63
COS[a]	"	1.30	0.92	1.91	0.78
MS[a]	"	0.94	1.29	0.62	0.68
FS[a]	"	1.33	1.20	1.92	1.74
VFS[a]	"	1.05	1.38	1.40	1.23
SILT	"	2.22	1.80	1.34	1.52
COSI[a]	"	1.66	1.92	0.49	1.24
FSI[a]	"	1.29	1.05	0.82	0.65
CLAY	"	0.83	0.56	0.66	1.08
PH_H20	pH units	0.092	0.123	0.077	0.126
PH-002M	"	0.064	0.042	0.039	0.060
PH-01M	"	0.093	0.032	0.142	0.125
CA-CL	meq/100g	0.232	0.326	0.044	0.032
MG_CL	"	0.063	0.033	0.127	0.121
K_CL	"	0.014	0.013	0.007	0.012
NA_CL	"	0.020	0.015	0.022	0.009
CA_OAC	meq/100g	0.289	0.474	0.029	0.030
MG_OAC	"	0.109	0.112	0.015	0.011
K_OAC	"	0.014	0.011	0.007	0.015
NA_OAC	"	0.023	0.013	0.013	0.011
CEC_CL	meq/100g	0.82	0.84	0.44	1.11
CEC_OAC	"	2.15	1.64	0.89	1.78
AC_KCL	"	0.40	0.27	0.13	0.22
AC_BACL	"	2.66	2.51	1.23	2.09
AL_KCL	"	0.40	0.27	0.20	0.21
CA_CL2	meq/100g	0.030	0.035	0.028	0.067
MG_CL2	"	0.008	0.018	0.016	0.013
K_CL2	"	0.005	0.003	0.002	0.002
NA_CL2	"	0.008	0.007	0.002	0.002
FE_CL2	"	0.003	0.002	0.001	0.003
AL_CL2	"	0.011	0.008	0.006	0.008
FE_PYP	wt %	0.063	0.078	0.024	0.031
AL_PYP	"	0.051	0.029	0.030	0.023
FE_AO	"	0.090	0.062	0.094	0.107
AL_AO	"	0.222	0.075	0.036	0.064
FE_CD	"	0.150	0.064	0.053	0.106
AL_CD	"	0.058	0.042	0.021	0.037
SO4_H2O	mg S/kg	1.60	3.08	0.88	0.89
SO4_PO4	"	8.50	5.04	2.93	3.91
SO4_0	mg S/L	0.17	0.11	0.09	0.11
SO4_2	"	0.14	0.20	0.11	0.16
SO4_4	"	0.29	0.22	0.18	0.21
SO4_8	"	0.25	0.24	0.21	0.43
SO4_16	"	0.56	0.45	0.53	0.81
SO4_32	"	1.00	1.59	0.84	1.22
C_TOT	wt %	0.48	0.23	0.21	0.19
N_TOT	"	0.027	0.018	0.009	0.013
S_TOT	"	0.0057	0.0050	0.0050	0.0057

[a] No data quality objective was established for this parameter.

Table 3-12. Summary of Within-Batch and Between-Batch Precision Estimates for the Parameter Groups

Parameter Group	Within-Batch[a] Sampling δ values	Within-Batch[a] Preparation δ values	Within-Batch[a] Analytical δ values	Between-Batch[b] Analytical SD
Particle size	1.41 (0.47)	1.35 (0.49)	1.15 (0.48)	1.10 (0.38)
Soil pH	0.083(0.013)	0.066(0.041)	0.086(0.043)	0.103(0.031)
Cations in NH4Cl	0.082(0.088)	0.097(0.133)	0.050(0.046)	0.044(0.046)
Cations in NH4OAC	0.109(0.110)	0.153(0.190)	0.016(0.008)	0.017(0.008)
CEC and Acidities	1.29 (0.94)	1.11 (0.86)	0.58(0.42)	1.08 (0.78)
Cations in CaCl2	0.011(0.009)	0.011(0.011)	0.009(0.009)	0.035(0.048)
Ext. Fe, Al	0.106(0.062)	0.058(0.017)	0.043(0.025)	0.062(0.035)
Ext. SO4, isotherms	1.56 (2.66)	1.37 (1.69)	0.72(0.88)	0.97 (1.17)
Total CNS	0.117(0.219)	0.084(0.103)	0.075(0.096)	0.070(0.085)

[a] Pooled delta values and standard deviations by parameter group.
[b] Pooled standard deviations and standard error by parameter group.

calcium chloride, the sulfate isotherm parameters, and total C, N, and S. For the Bs audit sample, laboratory differences were highly significant for NA_CL2, FE_CL2, and AL_CL2. For the Bw audit sample NA_CL2, laboratory differences were highly significant for VFS, CEC_CL, CA_CL2, and AL_CD. For the C audit sample, laboratory differences were highly significant for CA_CL2. Of the 13 cases of high significance, six were for cations in 0.002M CA_Cl2.

Differences Among Laboratories for Pooled Audit Samples

Table 3-14 shows the differences (columns 1 to 4) and rank (columns 5 to 8) for the 51 parameters pooled over the audit samples for each of the four laboratories. Each parameter was pooled for only the Bs and Bw horizons because all laboratories did not analyze the Oa, A, and C audit samples.

For the physical parameters, SP_SUR, VFS, and CLAY showed the highest interlaboratory differences, while SAND and FSI showed the lowest differences. For pH, all interlaboratory differences were low. The laboratories performed best on the pH parameters. For cations in ammonium chloride, NA_CL showed the highest differences and CA_CL showed the lowest differences. For cations in ammonium acetate, NA_OAC showed the highest differences and MG_OAC showed the lowest differences. For the two CEC parameters, the laboratories showed the highest differences for CEC_CL. For the acidity and aluminum parameters, the laboratories showed the highest differences for AL_KCL. For cations in 0.002M calcium chloride, the laboratories showed the highest differences for CA_CL2 and the lowest differences for NA_CL2. For iron and aluminum in the three extracts, the laboratories showed the highest differences for the dithionite extraction and the lowest differences for the pyrophosphate extraction. For the two extractable sulfates, and for the sulfate isotherm parameters, all laboratory differences were very low. For total elemental analysis, S_TOT showed the highest differences and N_TOT showed the lowest differences.

The highest differences for the physical parameters, cation exchange capacity, exchangeable acidity, and the extractable iron and aluminum parameters, were shown by Laboratory 3. The highest differences for the pH and total C, N, and S parameters were shown by Laboratory 1. The highest differences for the exchangeable cations in ammonium chloride and ammonium acetate, and for extractable cation in calcium chloride, were shown by Laboratory 2. The highest differences for the sulfate parameters were shown by Laboratory 4. For the 51 parameters, Laboratory 3 showed the highest differences overall.

The lowest differences for the physical parameters, exchangeable cations in ammonium chloride, ammonium acetate, and calcium chloride, and the extractable iron and aluminum parameters, were shown by Laboratory 4. The lowest differences for the sulfate and total C, N, and S parameters were shown by Laboratory 2. The lowest differences for the cation exchange capacity and acidity parameters were shown by Laboratory 1. The lowest differences for the pH parameters were shown

Table 3-13. Significant Interlaboratory Differences Between Laboratories by Parameter and Audit Sample Type

Parameter[a]	Audit Sample				
	Oa	A	Bs	Bw	C
MOIST			3 < 4	1 < 2,4	
SP_SUR			1 < 3		1 < 4
SAND		1 < 2[b]		1,3,4 < 2 1 < 4	
MS		1 < 2	1 < 4		2 < 4
FS		1 < 2			
VFS		1 < 2		1,3,4 < 2 **[c] 1 < 4 **	
SILT		2 < 1		2 < 3,4 < 1	
COSI		2 < 1		2 < 1,3,4	
FSI		2 < 1			
CLAY			1,3,4 < 2		
PH_H20			1 < 2,3,4	1 < 2	1 < 2
PH_01M		2 < 1			
CA_CL		2 < 1			
MG_CL	1 < 4				
NA_CL		2 < 1			
MG_OAC			2 < 1		
K_OAC		2 < 1	1,2,4 < 3		
NA_OAC				2 < 1,3	2,4 < 1
CEC_CL		2 < 1	1,2,4 < 3	2,4 < 1 ** 1 < 3 **	
CEC_OAC		2 < 1		2 < 1, 3 4 < 3	2,4 < 1
AC_KCL		1 < 2	3 < 4		4 < 1
AL_KCL	1,2 < 4 **	1 < 2		2 < 1,3,4 1 < 4	1 < 4
CA_CL2	1 < 2,4 **		1,3 < 2,4	1,3 < 2,4 **	1 < 2,4 **
MG_CL2			3 < 2	1 < 2	
K_CL2	1 < 4		3,4 < 2		1 < 4
NA_CL2			3 < 4		
FE_CL2			1,3,4 < 2 **		
AL_CL2	1 < 4 **		1 < 2,4 ** 3 < 4 **		
FE_AO		1 < 2			
AL_AO		1 < 2	1,3,4 < 2		
FE_CD				2 < 3	
AL_CD				1 < 3 **	
S04_P04					4 < 1
S04_2	4 < 1,2				
S04_4	4 < 1	1 < 2			
S04_8		1 < 2		4 < 1,2,3	
S04_16	2,4 < 1				
C_TOT	1 < 2,4		2,3,4 < 1		
N_TOT	1 < 2		2,3,4 < 1		
S_TOT	4 < 1,2		2,3,4 < 1		

[a] No significant differences were identified for VCOS, COS, PH_002M, K_CL, CA_OAC, AC_BACL, FE_PYP, AL_PYP, SO4_H20, SO4_0, SO4_32.

[b] 1, 2, 3, and 4 are contract laboratories.

[c] Significant at the 99 percent level of confidence.

Table 3-14. Relative Difference and Rank by Laboratory and Mean Laboratory Difference by Audit Sample Type

Parameter	Difference (%) Laboratory				Rank Laboratory				Difference (%) Audit Sample				
	1	2	3	4	1	2	3	4	Oa	A	Bs	Bw	C
MOIST	6	3	12	7	2	1	4	3	18	2	6	7	11
SP_SUR	16	9	22	8	3	2	4	1	nd[a]	33	14	10	57
SAND	5	4	2	1	4	3	2	1	nd	4	1	12	1
VCOS	2	5	4	7	1	3	2	4	nd	1	5	4	3
COS	6	5	12	3	3	2	4	1	nd	1	6	5	1
MS	2	6	5	6	1	4	2	3	nd	3	5	4	3
FS	4	3	5	4	2	1	4	3	nd	7	3	11	3
VFS	26	25	18	2	4	3	2	1	nd	3	8	24	6
SILT	8	7	1	2	4	3	1	2	nd	8	2	6	18
COSI	15	14	3	2	4	3	2	1	nd	12	4	12	18
FSI	1	2	3	1	1	3	4	2	nd	6	5	1	7
CLAY	7	16	14	24	1	3	2	4	nd	2	37	12	60
PH_H2O	1.7	0.9	0.5	0.1	4	3	2	1	2.5	0.1	0.9	1.0	2.4
PH_002M	1.1	0.1	0.1	0.7	4	2	1	3	1.2	0.2	0.2	0.6	0.8
PH_01M	0.9	0.8	0.1	0.3	4	3	1	2	0.3	0.8	1.3	0.8	1.2
CA_CL	9	11	4	6	3	4	1	2	21	7	9	8	13
MG_CL	4	9	15	14	1	2	4	3	21	1	11	8	5
K_CL	11	15	6	7	3	4	1	2	10	1	23	2	11
NA_CL	71	38	49	10	4	2	3	1	2	28	44	38	–[b]
CA_OAC	16	10	8	4	4	3	2	1	12	5	7	11	11
MG_OAC	8	12	7	3	3	4	2	1	14	3	11	3	3
K_OAC	18	22	21	1	2	4	3	1	10	4	14	16	18
NA_OAC	9	35	54	14	1	3	4	2	9	13	30	35	–
CEC_CL	14	20	57	9	2	3	4	1	7	41	8	25	8
CEC_OAC	9	12	12	3	2	4	3	1	1	10	7	13	22
AC_KCL	4	3	16	8	2	1	4	3	43	10	8	2	15
AC_BACL	1	2	16	8	1	2	4	3	10	3	6	3	31
AL_KCL	4	9	14	19	1	2	3	4	44	13	11	12	37
CA_CL2	25	15	26	17	3	1	4	2	56	4	16	23	16
MG_CL2	15	21	19	3	2	4	3	1	39	17	13	15	44
K_CL2	14	20	17	5	2	4	3	1	40	1	12	17	9
NA_CL2	6	9	20	7	1	3	4	2	29	1	10	7	–
FE_CL2	22	34	10	15	3	4	1	2	52	14	21	–	–
AL_CL2	22	4	17	24	3	1	2	4	53	8	16	–	–
FE_PYP	2	3	7	6	1	2	4	3	19	5	4	4	4
AL_PYP	9	1	2	7	4	1	2	3	9	7	2	6	4
FE_AO	7	6	8	4	3	2	4	1	9	10	8	4	20
AL_AO	4	10	12	3	2	3	4	1	11	17	10	2	1
FE_CD	3	7	24	4	1	3	4	2	4	19	8	7	7
AL_CD	12	8	9	6	4	2	3	1	8	2	6	12	10
SO4_H2O	5	3	8	4	3	1	4	2	3	3	9	2	13
SO4_PO4	8	2	3	4	4	1	2	3	8	2	7	3	20
SO4_0	3	3	3	5	3	1	2	4	3	0.4	4	3	7
SO4_2	2	2	4	2	2	1	4	3	5	3	2	2	3
SO4_4	2	4	1	2	2	4	1	3	4	4	1	4	2
SO4_8	1	3	3	5	1	3	2	4	4	4	1	5	1
SO4_16	2	4	2	3	2	4	1	3	4	4	2	5	1
SO4_32	0.4	1	3	2	1	2	4	3	8	1	1	2	1
C_TOT	21	3	13	9	4	1	3	2	10	4	14	2	12
N_TOT	14	6	7	5	4	2	3	1	15	6	12	5	–
S_TOT	22	10	5	22	3	2	1	4	9	12	24	7	–

[a] Physical parameters were not determined in the organic (Oa) soil audit sample.

[b] Concentrations are too low for meaningful difference estimates.

by Laboratory 3. For the 51 parameters, Laboratory 4 showed the lowest differences overall.

The reasons for the above interlaboratory differences are not readily discernible. Each laboratory appears to have its analytical strengths and weaknesses which probably relate to laboratory experience in specific analysis, instrumentation capability, management initiatives, staffing issues, and priority in analytical commitments. A higher degree of difficulty for a specified method would tend to cause larger accuracy and precision problems for the laboratories and larger interlaboratory differences would result for these parameters. The laboratories also performed differently on the audit samples. This showed that some soils, e.g. the C horizon with its low concentration levels for the available extractable and exchangeable cations, were analyzed by the laboratories with greater difficulty.

Differences Among Audit Samples for Pooled Laboratories

Table 3-14 also shows the mean laboratory differences (columns 9 to 13) for the 51 parameters pooled over the four laboratories for each audit sample.

For the Oa audit sample, the laboratories showed the highest differences for cations in calcium chloride and the acidities. For the A audit sample, the laboratories showed the highest differences for CEC and acidities. For the Bs audit sample, the laboratories showed the highest differences for the cations in ammonium chloride and ammonium acetate. For the Bw audit sample, the laboratories showed the highest differences for the cations in ammonium acetate and 0.002M calcium chloride. For the C audit sample, the laboratories showed the highest differences for the acidities. For the Oa, A, Bs, Bw, and C audit samples, the laboratories showed the lowest differences for pH and the sulfate isotherm parameters.

Representativeness

All pedons sampled were within the range of morphological characteristics outlined in their respective sampling classes (Coffey et al., 1987). Hence, the DQO for representativeness of the field sampling was satisfied.

The homogenization and subsampling procedures at the preparation laboratories produced representative analytical soil samples of known and accepted quality (Papp and Van Remortel, 1987). More information on this characteristic of the data can be found in the precision discussions of this report, where assessments of the preparation duplicates are made.

Histograms of the range and frequency distribution of the routine samples, field duplicates, preparation duplicates, and natural audit samples for each of the parameters are presented in Appendix F. The field duplicates and preparation duplicates were not always representative of the range and frequency distribution of analyte concentrations for the routine samples (see Table 3-15). A less standardized selection method for the preparation duplicates, compared to that of the DDRP Southern Blue Ridge Province Soil Survey, was responsible for poor representativeness in the PD data set. The preparation laboratory personnel chose those samples which had ample soil when selecting a sample for the preparation duplicate. The soil types which were not well represented volume-wise were not usually selected for duplicate samples. Therefore, their selection was inadvertently biased in preference of sample types which, unfortunately had larger volumes. The audit samples generally were representative of the range of data from the routine samples.

Completeness

Soil sampling protocols specified the sampling of all of the designated pedons. A total of 306 pedons were sampled of the 319 pedons initially selected, resulting in 95.9 percent completeness (Coffey et al., 1987).

As specified in the protocols, each batch of samples sent to a analytical laboratory contained a preparation duplicate sample. The requested soil analyses and sample processing tasks were performed on 100 percent of the bulk samples and clods received by the preparation laboratories (Papp and Van Remortel, 1987).

Verified Data Base

The AO and JJ flags (denoting missing data or insufficient sample for analysis,

Table 3-15. Significant Differences in Distribution of Field and Preparation Duplicates Relative to Routine Samples

Parameter	Data Set[a]	n	Mean	p05[b]	p50[b]	p95[b]	KS-Stat[c]
MOIST	RS	1,634	2.79	0.25	1.54	8.86	—
	FD	270	2.71	0.33	1.72	8.49	0.093
	PD	55	1.17	0.20	0.78	4.13	0.323
SP_SUR	RS	1,353	26.63	2.69	20.64	67.29	—
	FD	241	29.83	3.09	24.24	74.29	0.207
	PD	55	17.37	1.74	14.46	44.41	0.222
SAND	RS	1,352	62.30	26.03	63.65	95.77	—
	FD	241	59.09	24.43	59.00	93.50	0.208
	PD	55	70.35	29.80	75.90	98.02	0.414
VCOS	RS	1,353	6.73	0.50	5.50	16.60	—
	FD	241	6.11	0.30	4.90	14.92	0.207
	PD	55	6.52	0.16	5.20	17.82	0.274
COS	RS	1,353	11.25	1.60	9.20	28.23	—
	FD	241	10.33	1.61	8.40	27.76	0.207
	PD	55	12.23	1.22	12.10	31.66	0.389
MS	RS	1,353	14.08	2.60	12.60	31.80	—
	FD	241	12.69	2.71	11.20	29.86	0.207
	PD	55	16.69	2.02	15.00	35.96	0.366
FS	RS	1,353	16.89	4.20	16.00	32.89	—
	FD	241	15.99	3.43	15.10	32.11	0.207
	PD	55	20.27	5.66	19.30	46.12	0.414
VFS	RS	1,353	13.30	2.90	12.70	25.10	—
	FD	241	13.91	2.64	13.50	26.36	0.207
	PD	55	14.63	1.64	13.30	33.28	0.329
SILT	RS	1,352	30.97	3.30	30.50	58.20	—
	FD	241	33.80	6.12	35.10	58.75	0.208
	PD	55	23.86	0.60	21.20	53.64	0.208
COSI	RS	1,353	14.33	2.07	14.00	27.90	—
	FD	241	15.59	3.50	15.40	30.79	0.207
	PD	55	11.88	0.06	11.10	25.48	0.207
FSI	RS	1,353	16.65	1.20	14.40	37.83	—
	FD	241	18.21	2.01	16.80	38.21	0.207
	PD	55	11.97	0.96	8.00	31.90	0.229
CLAY	RS	1,352	6.76	0.40	4.10	21.00	—
	FD	241	7.18	0.51	4.60	23.65	0.208
	PD	55	5.79	0.20	2.90	22.28	0.232
PH_H2O	RS	1,634	4.86	3.48	4.87	6.34	—
	FD	270	4.89	3.63	4.84	6.40	0.105
	PD	55	5.25	4.02	5.15	6.56	0.258
PH_002M	RS	1,632	4.45	3.16	4.48	5.64	—
	FD	270	4.48	3.33	4.45	5.71	0.110
	PD	54	4.72	3.59	4.71	5.61	0.225
PH_01M	RS	1,634	4.25	2.86	4.31	5.47	—
	FD	270	4.30	3.02	4.29	5.44	0.097
	PD	55	4.56	3.46	4.53	5.48	0.225
CA_CL	RS	1,633	3.50	0.01	0.31	17.73	—
	FD	269	3.51	0.01	0.19	18.64	0.090
	PD	55	0.87	0.01	0.09	4.48	0.193

(continued)

Table 3-15. Continued

Parameter	Data Set[a]	n	Mean	p05[b]	p50[b]	p95[b]	KS-Stat[c]
MG_CL	RS	1,633	0.79	0.00	0.07	3.69	—
	FD	269	0.62	0.00	0.04	3.48	0.107
	PD	55	0.34	0.00	0.02	1.61	0.188
K_CL	RS	1,633	0.20	0.01	0.06	1.14	—
	PD	55	0.05	0.00	0.03	0.18	0.252
NA_CL	RS	1,633	0.08	0.00	0.03	0.32	—
	PD	55	0.03	-0.01	0.02	0.10	0.196
CA_OAC	RS	1,633	3.08	0.01	0.30	15.43	—
	PD	55	0.79	0.01	4.74	0.11	0.196
MG_OAC	RS	1,633	0.69	0.00	0.08	3.53	—
	FD	269	0.59	0.00	0.04	3.53	0.109
	PD	55	0.31	0.00	0.03	1.44	0.190
K_OAC	RS	1,633	0.22	0.01	0.06	1.23	—
	PD	55	0.05	0.00	0.03	0.14	0.275
NA_OAC	RS	1,633	0.09	0.00	0.02	0.35	—
	PD	55	0.02	-0.02	0.02	0.07	0.225
CEC_CL	RS	1,633	11.28	0.55	5.81	41.11	—
	PD	55	3.95	0.51	3.11	12.12	0.321
CEC_OAC	RS	1,632	26.26	1.02	10.38	111.70	—
	PD	55	7.03	0.70	5.51	20.66	0.340
AC_KCL	RS	1,634	3.11	0.02	1.53	11.65	—
	PD	55	1.24	0.00	0.52	4.92	0.278
AC_BACL	RS	1,634	28.36	0.80	12.46	111.24	—
	PD	55	8.19	-0.02	4.86	29.88	0.324
AL_KCL	RS	1,633	2.10	0.02	1.13	7.63	—
	PD	54	1.01	-0.06	0.45	4.48	0.237
CA_CL2	RS	1,633	0.88	0.28	0.61	2.82	—
	FD	269	0.78	0.32	0.59	2.77	0.096
MG_CL2	RS	1,633	0.17	0.00	0.04	0.90	—
	FD	269	0.12	0.00	0.03	0.77	0.115
	PD	55	0.05	0.00	0.02	0.21	0.224
K_CL2	RS	1,633	0.08	0.00	0.01	0.61	—
	PD	55	0.01	0.00	0.01	0.03	0.267
NA_CL2	RS	1,633	0.06	0.01	0.02	0.23	—
	PD	55	0.02	0.00	0.02	0.07	0.265
FE_CL2	RS	1,633	0.01	0.00	0.00	0.07	—
	FD	269	0.00	0.00	0.00	0.03	0.225
	PD	55	0.00	0.00	0.00	0.03	0.213
AL_CL2	RS	1,633	0.07	0.00	0.02	0.31	—
	PD	55	0.03	-0.01	0.01	0.18	0.203
FE_PYP	RS	1,633	0.33	0.01	0.15	1.16	—
	FD	270	0.37	0.02	0.21	1.19	0.125
	PD	55	0.18	0.01	0.06	0.84	0.227
AL_PYP	RS	1,633	0.34	0.03	0.19	1.09	—
	FD	270	0.41	0.03	0.30	1.19	0.158
	PD	55	0.22	0.02	0.11	0.84	0.201

(continued)

Table 3-15. Continued

Parameter	Data Set[a]	n	Mean	p05[b]	p50[b]	p95[b]	KS-Stat[c]
FE_AO	RS	1,634	0.48	0.03	0.27	1.56	—
	FD	270	0.54	0.04	0.34	1.60	0.094
	PD	55	0.31	0.01	0.20	1.35	0.228
AL_AO	RS	1,634	0.54	0.04	0.26	1.89	—
	FD	270	0.73	0.05	0.40	2.26	0.141
AL_CD	RS	1,632	0.36	0.03	0.20	1.27	—
	FD	270	0.43	0.04	0.28	1.40	0.152
	PD	55	0.21	0.03	0.13	0.93	0.212
SO4_H2O	RS	1,634	17.34	1.70	8.45	56.05	—
	PD	55	7.19	1.27	4.79	22.12	0.278
SO4_PO4	RS	1,631	45.27	2.28	23.84	161.95	—
	FD	270	53.18	2.65	33.31	168.67	0.119
	PD	54	23.49	2.28	10.05	104.69	0.284
SO4_0	RS	1,633	2.77	0.24	0.94	9.86	—
	PD	55	0.70	0.13	0.68	1.61	0.294
SO4_2	RS	1,633	4.25	1.45	2.42	12.08	—
	PD	55	2.19	1.46	2.25	2.95	0.315
SO4_4	RS	1,633	5.84	2.40	4.05	14.87	—
	FD	270	5.42	2.29	3.89	13.85	0.096
	PD	55	3.73	2.75	3.81	4.43	0.314
SO4_8	RS	1,633	9.12	4.45	7.61	18.20	—
	FD	270	8.49	4.17	7.23	18.37	0.118
	PD	55	7.08	5.22	7.21	8.49	0.262
SO4_16	RS	1,634	16.25	9.44	15.03	26.45	—
	FD	270	15.82	8.50	14.15	24.21	0.145
	PD	55	14.30	10.93	14.56	16.59	0.250
SO4_32	RS	1,634	30.69	20.80	30.10	42.35	—
	FD	270	29.73	18.97	28.89	38.62	0.152
	PD	55	28.93	21.77	29.50	32.77	0.205
C_TOT	RS	1,633	8.18	0.06	1.48	46.68	—
	FD	270	6.51	0.10	1.95	47.44	0.114
	PD	55	0.96	0.04	0.33	5.31	0.362
N_TOT	RS	1,633	0.33	0.00	0.07	1.71	—
	FD	270	0.27	0.00	0.10	1.63	0.094
	PD	55	0.06	-0.03	0.02	0.23	0.397
S_TOT	RS	1,634	0.05	0.00	0.01	0.22	—
	FD	270	0.04	0.00	0.02	0.24	0.206
	PD	55	0.01	0.00	0.01	0.03	0.283

[a] RS = routine samples, FD = field duplicates, and PD = preparation duplicates.

[b] p05, p50, and p95 are the 5th, 50th, and 95th percentiles by data set.

[c] Kolmogorov-Smirnov test; statistics are significant at the 0.05 level for the critical value: FD_RS = 0.089, PD_RS = 0.186.

NOTE: There were no significant differences identified for FE_CD.

respectively [see Appendix A]) were assigned to the 1,634 routine samples to assess analytical completeness of the verified data base. The DQO for analytical completeness of 90 percent or higher was satisfied for all parameters (see Table 3-16).

Validated Data Base

Five levels of confidence, ranging from 0 to 4, were used to segregate and classify data in the validated data base. Levels of confidence of 2 or less, i.e., less than two major flags or less than one major and two minor flags assigned per sample, were used to assess completeness in the validated data base (see Table 3-16).

Comparability

The entire verified data base was used for the assessment of data quality for both

Table 3-16. Completeness of Soil Analysis Using Data for Routine Samples from the Verified and Validated Data Bases

Parameter	Verified data base[a]		Validated data base[a]	
	n	percent	n	percent
MOIST	1,634	100.0	1,632	99.9
SP_SUR	1,353	99.9	1,344	99.3
SAND, SILT, CLAY	1,352	99.9	1,351	99.8
PH_H20	1,634	100.0	1,631	99.8
PH_002M	1,632	99.9	1,628	99.6
PH_01M	1,634	100.0	1,631	99.8
CA_CL	1,633	99.9	1,555	95.2
MG_CL	1,633	99.9	1,528	93.5
K_CL	1,633	99.9	1,595	97.6
NA_CL	1,633	99.9	1,450	88.7
CA_OAC	1,633	99.9	1,577	96.5
MG_OAC	1,633	99.9	1,556	95.2
K_OAC	1,633	99.9	1,582	96.8
NA_OAC	1,633	99.9	1,464	89.6
CEC_CL	1,633	99.9	1,525	93.3
CEC_OAC	1,632	99.9	1,566	95.8
AC_KCL	1,634	100.0	1,547	94.7
AC_BACL	1,634	100.0	1,582	96.8
AL_KCL	1,633	99.9	1,569	96.0
CA_CL2	1,633	99.9	1,610	98.5
MG_CL2	1,633	99.9	1,599	97.9
K_CL2	1,633	99.9	1,603	98.1
NA_CL2	1,633	99.9	1,594	97.6
FE_CL2	1,633	99.9	1,032	63.2
AL_CL2	1,633	99.9	1,404	85.9
FE_PYP	1,633	99.9	1,609	98.4
AL_PYP	1,633	99.9	1,618	99.0
FE_AO	1,634	100.0	1,613	98.7
AL_AO	1,634	100.0	1,628	99.6
FE_CD	1,632	99.9	1,623	99.3
AL_CD	1,632	99.9	1,619	99.1
SO4_H2O	1,633	99.9	1,568	96.0
SO4_PO4	1,630	99.8	1,492	91.3
SO4_0	1,633	99.9	1,577	96.5
SO4_2	1,633	99.9	1,630	99.8
SO4_4	1,633	99.9	1,630	99.8
SO4_8	1,633	99.9	1,632	99.9
SO4_1,6	1,634	100.0	1,630	99.8
SO4_32	1,634	100.0	1,631	99.8
C_TOT	1,633	99.9	1,606	98.3
N_TOT	1,633	99.9	1,527	93.5
S_TOT	1,633	99.9	1,312	80.3

[a] The total of routine samples (N) was 1,634; for the verified data base, n is the number of samples which underwent analysis; for the validated data base, n is the number of samples that are valid at a level of confidence of 2 or less; (Note: 280 of the routine samples were organic soils that were not required to undergo specific surface or particle size analyses; in these cases, N = 1,354).

the Northeastern and SBRP surveys because the indiscriminate use or non-use of flagged data was felt to be inappropriate for the purposes of quality assessment. The flags were applied in order to caution the data user that certain data points are suspect and may not be suitable for a particular type of data analysis.

Comparison of Analytical and Sample Preparation Methods

The preliminary audit sample data provided by three independent referee laboratories prior to the initiation of the DDRP surveys could not be utilized. This was due to differences in following analytical protocols by the referee laboratories, e.g., one laboratory analyzed seven replicates at one time rather than seven replicates analyzed separately. Sufficient audit sample data were available from the DDRP contract laboratory analyses, however, to provide an estimate of the audit sample composition. These data were used in the assessment of precision, interlaboratory differences, and comparability.

Difficulties were encountered in developing and evaluating the analytical methods prior to initiation of the DDRP surveys. As a result, there are certain instances where the methods actually used by the contract laboratories differ from those specified in the DDRP Analytical Methods Manual or in the individual laboratory solicitations (Cappo et al., 1987). Approval for methods amendments was given only when it was determined by the QA staff that these changes would not significantly affect the analytical results. Methods amendments were recorded in an operations log book by QA staff but did not always result in an official EPA contract modification.

During the Northeastern survey, analytical methods for two parameters were changed sufficiently to warrant reanalysis of all previously analyzed samples. The laboratories were contracted to reanalyze all of their samples for AL_KCL by using a method which employed HCL rather than H_2SO_4 in the acidification step. Two of the laboratories also were contracted to adjust the soil:solution ratio for PH_002M and to reanalyze all of the samples; the third laboratory already had been using the amended ratio. Hence, reanalyses have corrected all data significantly affected by methods amendments which occurred as the Northeastern survey progressed.

Identical soil preparation methods were used in preparing soil samples for the two surveys. The protocols were revised for clarity in the SBRP survey but the methods remained comparable. The procedure for selecting a preparation duplicate for each batch was refined for the SBRP survey, resulting in better representativeness of the preparation duplicates.

Comparison of Field Sampling Methods

It was discovered that the field duplicates in the Northeastern survey were sampled by two different methods, i.e., some crews placed alternate portions of soil from the same horizon into separate bags (the alternate trowel method) while other crews collected the total amount of sample, performed a simple homogenization, and split the sample. The alternate trowel method was used in order to determine sampling variability.

Although the written protocols provided to the Northeastern sampling crews specified an alternate trowel method for the field duplicate, verbal instructions at the pre-sampling training workshop were to collect a composite sample from a horizon and create a split of this material to serve as the duplicate. Later clarification to each of the sampling crews reinforced the alternate trowel procedure as the intended method. By this time, however, some of the field duplicates had already been sampled by the split sample procedure.

As a result of information gathered during the Northeastern survey, the sampling protocols were clarified in order to address contamination issues and the collection of field duplicates for the SBRP survey. Field duplicates for the SBRP sites were sampled using only the alternate trowel method. The data from samples collected by the alternate trowel method are expected to be more variable than the data from samples collected by the split sample method. Because of the inconsistent application of the sampling method, the variances for the field duplicates for the Northeastern survey tend to fluctuate among pedons. Thus, overall within-batch variability was expected to be greater in the SBRP than in the Northeastern survey because of the additional sampling variability error contained in the field duplicates that were sampled using the alternate trowel method. This does suggest that measurement error in the Northeastern survey may have been somewhat underestimated. However, it does not mean that the routine data between regions are not comparable. The same methodology was used for routine soil sampling in each survey. The field sampling audit team did not report any deviations from the sampling protocols that would compromise the integrity of the routine data.

Comparison of Audit Sample Distribution

Although the Northeastern survey was a more extensive survey in terms of the total number of samples collected, only one pair of natural audit samples was placed in each batch in contrast to two pairs per batch in the SBRP survey. This accounts for the similar total number of audit samples (112 versus 104, respectively), even though the number of batches in each survey differed greatly. The soil for each audit type in both regions came from the same bulk audit sample. Therefore, data for each audit sample can be compared between the two surveys for any given parameter. Significant differences could then be attributed to differing amounts of measurement error.

Interlaboratory Comparison Study

The study uses data from the DDRP audit samples to compare the results of analytical methods used in the NE and SBRP surveys to those currently in use at 17 selected soil characterization laboratories throughout the United States and Canada (Fenstermaker et al., in preparation).

Section 4

Conclusions and Recommendations

Data Verification

Verification of Data Packages

A number of improvements can be made in the verification procedure. *It is recommended that a computerized data entry and verification system be developed that will calculate all of the final data values and produce a list of flags and data entry errors.* This will provide a much faster recycling time for submission of data packages and completion of the data review phase and confirmation/reanalysis requests. All raw data needed to calculate final values could be entered and a calculation program could be run. This would facilitate the rapid identification of entry errors and ultimately reduce the amount of reanalysis needed. *It is recommended that a computer link between the laboratories and the quality assurance staff be established that will enable the transfer of preliminary and final data. It is further recommended that the verification program be designed to evaluate the quality control checks and other contractual requirements, thereby inducing the laboratories to assume much of the responsibility for identification and correction of errant data.* This would result in the extensive use of quality control charts in order to 1) reduce between-batch and between-laboratory error and 2) provide ongoing records for later QA assessment.

It is recommended that evaluation of the blind audit samples be made part of the computer verification system. However, this portion of the system would be accessible only to the quality assurance staff. This evaluation would be used in conjunction with the quality control and summary checks to determine the acceptance of batches from the laboratories.

Internal Consistency

The internal consistency checks of routine data for each analytical parameter were performed during the final weeks of data verification for the Northeastern Soil Survey. Outliers determined by the internal consistency computer program were checked only for transcription errors. The program generated outliers consisting of approximately one percent of the total number of data values for each parameter. Of these outliers, approximately 10 percent, i.e., 0.1 percent of the total data values, were found to be in error. A few parameters did contain a relatively large number of outliers which, after correction, improved the quality of data.

There were some parameters that did not correlate well with any of the other parameters. Although the highest and lowest one percent of these values for these parameters were reviewed, *it is recommended that a better procedure for checking these values be developed.*

The internal consistency checks could provide useful information during the earlier stages of verification. These data can be used to influence requests for reanalysis. *It is recommended that the internal consistency checks become an integral part of the verification process.* Difficulties with methodology and data reporting become apparent when significant numbers of outliers are found for specific batches.

If it can be determined that parameter correlations are comparable among regions of study, then single batches of data from new study regions can be incorporated into an overall data file and reviewed to distinguish outliers for the region of new study. However, if the correlations do not compare across regions, a statistically significant population of data must be collected from the new region before suspect data points from individual batches can be viewed as outliers.

It is recommended that a method to identify confirmed outlying data points be developed. These data tend to distort the data quality assessment. In addition to the present internal consistency checks, *it is also recommended that a suitable statistical analysis be selected to identify which data points are disproportionately influencing the overall data.* These data points and any associated routine data could be highlighted with a special flag for the benefit of data users.

Data Quality Objectives

Detectability

Considerable effort was expended during the course of this survey to evaluate and improve the detectability of various parameters. In particular, significant improvement was obtained for the exchangeable cations. *It is recommended that attention be given to improving detectability in future surveys.* Additional methods research is essential to this effort.

Data quality objectives for detectability were not set at the start of the survey with regard to system detection limits. Although instrument detection limits are an integral part of the detectability issue, the actual detection limit that can be applied to the final data set is the system detection limit and not the instrument detection limit. *It is recommended that both instrument detection and system detection limits be addressed in the data quality objectives for future surveys.*

It has been noted that soil blanks samples were not used in this survey. Therefore, it was difficult to calculate system detection limits or to identify when contamination may have occurred. Although some consideration has been given to the development of a soil blank sample, *it is recommended that low concentration audit samples, entered into the system during the sampling phase, be utilized as substitutes for soil blank samples.* These samples would serve not only to identify contamination problems and allow for the calculation of detection limits, but could also be used to estimate system precision and accuracy as well as provide additional quality control benefits.

Precision

The precision results indicate that the analytical within-batch precision objectives were satisfied in most cases. Occasionally, however, an objective was not met for an upper or lower tier of a parameter. Such parameters included sand, silt, calcium in ammonium chloride, total acidity, cations in calcium chloride, iron in acid oxalate, sulfate zero isotherm, and total nitrogen.

It was necessary to investigate why the laboratories had difficulty in satisfying certain precision objectives, e.g., the objectives might be unreasonably restrictive, the laboratories might have had problems with the methods, or there might have been sample preparation problems. Also, the disproportionate effect of inordinate data points on the estimates was investigated.

Table 4-1 is a summary of the overall achievement of the data quality objectives for analytical within-batch precision for the 42 parameters arranged into analytical groups. A precision index was determined for each group of parameters by pooling and weighting the standard deviations across each parameter within the group for the lower and upper tiers and dividing by their respective data quality objectives. These values were then summed and divided by the total degrees of freedom for the group. A precision index exceeding 1.0 (denoted by an asterisk in the table) indicates that the precision estimate for this parameter group did not meet the "overall objective" when viewed from the perspective of the entire concentration range, i.e., it exceeded the DQO. Values below 1.0 mean that the data quality objectives were met for the parameters in the group. The lower the precision index, the higher the precision for the range. This approach helped to identify which parameter groups should undergo further quality assurance emphasis in order to redefine the objectives for future surveys or to reassess the analytical procedures for the affected parameters. As a group, particle size analysis (SAND, SILT, and CLAY) and the extractable cations in 0.002M $CaCl_2$ exceeded the DQOs over the concentration range.

The lack of a two-tiered data quality objective for the particle size parameters might explain the relatively high variability, although it is also possible the objective could be somewhat restrictive. Additionally, factors, such as temperature, that influence

Table 4-1. Precision Indices Based on Pooled Within-Batch Precision Estimates for Parameter Groups Over Entire Concentration Range

Parameter group (parameters included)	Precision index
Particle size analysis (SAND, SILT, and CLAY)	1.21*
Soil pH (PH_: H2O, 002M, and 01M)	0.57
Exchangeable cations (CA_, MG_, K_, and NA_: CL)	0.64
Exchangeable cations (CA_, MG_, K_, and NA_: OAC)	0.49
Cation exchange capacity (CEC_CL and CEC_OAC)	0.68
Exchangeable acidity (AC_KCL, AC_BACL, and AL_KCL)	0.45
Extractable cations (CA_, MG_, K_, MG_, FE_, and AL_: CL2)	1.55*
Extractable iron and aluminum (FE_ and AL_: PYP, AO, and CD)	0.50
Extractable sulfate (SO4_: H20 and PO4)	0.43
Sulfate isotherms (SO4_: 0, 2, 4, 8, 16, and 32)	0.79
Elemental analysis (C_TOT, N_TOT, and S_TOT)	0.84

* Parameter group exceeded the specified data quality objectives

the gravimetric/sieve/pipet method, may have caused variability for size fractions present in low amounts. *It is recommended that an effort be made to locate an uncontaminated filter material for the determination of the basic cations or modify the pretreatment procedure for the filter material used. It is recommended that additional methods details be reviewed and provided where appropriate in order to reduce within-laboratory analytical variability. It is recommended that the DQO for SAND and SILT be increased from 1.0 percent to 3.0 percent. It is recommended that a two-tiered precision objective be defined for the extractable cations in calcium chloride.*

For calcium in ammonium chloride and for total acidity, several audit sample pairs having low concentration exhibited high variability which increased the imprecision for data below the knot. For total nitrogen, one laboratory exhibited significant interlaboratory differences which might explain the variability in the data.

As expected, increasing sources of confounded data collection error led to increased standard deviations in the precision estimates. Of the 66 cases where the precision estimates below and above the knot for the preparation duplicates were compared to the analytical data quality objectives, (see Tables 3-2 through 3-10, inclusive) only 31 cases exceeded the objective. This indicates that the preparation laboratories performed relatively well in subsampling the bulk soil samples. In many cases, the error estimates for the preparation duplicates were less than that for the audit samples. This suggests that the quality assurance staff may have had more difficulty in homogenizing the 500-kilogram bulk audit samples as compared to the 5.5-kilogram routine samples homogenized at the preparation laboratories. This has implications for the preparation of any future audit samples, but also reflects well on the subsampling procedure followed by the preparation laboratories. The audit samples were homogenized and subsampled using a modified cone-and-quartering technique (Schumacher et al., in preparation) and the preparation duplicates were homogenized and subsampled using a Jones-type riffle splitter.

For the field duplicates, 37 of the 66 cases exceeded the analytical data quality objectives. *It is recommended that specific data quality objectives be defined for system-wide measurement.* Data from the field duplicates could be used. In addition, the relatively low precision for the field duplicates for some parameter groups suggests that the component of error from soil sampling is a large portion of the data collection error. The alternate trowel method was meant to minimize the error due to spatial variability which is confounded with the soil sampling component in the data collection error. Also, as anticipated, the sampling class/horizon groups showed the highest levels of error due to inherent population variability.

Pooling of the analytical data across the mineral audit samples (A, Bs, Bw, and C) allows the inordinate effect of low concentration in the C audit samples to be included in the analytical error. Further pooling of the delta values for each parameter into parameter groups increases the difficulty in assessing trends for the within-batch components of error.

Accuracy (Interlaboratory Differences)

The approach taken for this report for evaluating bias was to assess interlaboratory differences for the 51 analytical parameters by comparing mean values among the individual laboratories and mean values for the laboratories combined across audit samples. The lack of acceptable or "true" analytical values for the soil parameters prohibited the assessment of accuracy, hence, interlaboratory differences are used to describe the relative systematic error. Three basic comparisons were made: (1) the use of a statistical test to directly compare laboratories, (2) pooling of audit sample data (Bs and Bw audit samples) for each laboratory to compare and rank overall laboratory performance, and (3) pooling data from each laboratory for each audit sample (Oa, A, Bs, Bw, and C horizons) to compare laboratory performance by audit sample type.

Significant Differences Among Laboratories

There were 150 cases out of 2,928 possible cases (five percent) where one laboratory was significantly different from another laboratory at the 0.05 level. These occurred in 17, 19, 43, 41, and 13 cases for the Oa, A, Bs, Bw, and C audit samples, respectively. Of the 2,928 cases, 24 (or 0.8 percent) were highly significant at the 0.01 level. The majority of these cases were in the Bw audit sample. Of all the parameter groups, cations in 0.002M calcium chloride had the largest number of highly significant differences.

Differences Among Laboratories

Table 4-2 shows the mean laboratory difference as percent for each laboratory and audit sample type for 50 parameters arranged for comparison purposes.

The lowest interlaboratory differences occurred for the soil pH parameter group. The laboratories showed the highest differences overall for the CEC and cations in ammonium chloride, followed closely by cations in 0.002M calcium chloride and cations in ammonium acetate. The mean interlaboratory differences across all parameters for laboratories 1, 2, 3, and 4 were 9.5, 9.3, 11.6, and 6.9 percent, respectively.

Differences Among Audit Samples

The laboratories showed the highest differences overall for the C audit sample and the lowest differences overall for the A audit sample (see Table 4-2). The mean interlaboratory differences for the Oa, A, Bs, Bw, and C audit samples were 13.8, 9.3, 14.5, 10.7, and 15.8 percent, respectively. It was noted that the C audit sample generally had the lowest concentrations for most of the parameters. The highest interlaboratory difference was in the Oa audit sample for cations in 0.002M calcium chloride and the lowest interlaboratory difference was in the A audit sample for pH.

No single laboratory was consistently superior to the others for all parameters or parameter groups. Each laboratory appears to have individual strengths in specific analytical methods, which is probably a reflection of the combination of experience, instrumentation, and laboratory management within each laboratory. This resulted in a patchwork of differences on a parameter group basis, although a general trend existed for the overall ranking of the laboratories.

In order to limit the interlaboratory differences in future surveys, *it is recommended that the DDRP staff consider the possibility of choosing laboratories to perform analyses on a parameter basis for those parameters or parameter groups that revealed inherently high differences or where specialized instrumentation is used, e.g., total C, N, and S.* One laboratory would analyze all soil samples for a given parameter or parameter group. This approach would require an advanced computerized quality assurance program as well as establishing acceptable data values for the audit samples in order to monitor laboratory performance.

It is recommended that a more stringent laboratory selection procedure be adopted in the pre-evaluation process for the selection of contract laboratories. Since one of the major goals of any quality assurance program is minimizing random and systematic errors, selection of the best possible laboratories is of primary importance. As shown, laboratories differ substantially in their overall performance for certain parameters.

It is recommended that a quality control soil audit sample be incorporated into the quality assurance program to better monitor the analytical results of the laboratories. A

Table 4-2. Summary of Interlaboratory Differences by Laboratory and Audit Sample Type

Parameter	n[a]	Interlaboratory difference (%)								
		Laboratory				Sample Type				
		1	2	3	4	Oa	A	Bs	Bw	C
Specific surface	1	6	9	22	8	nd[b]	3	4	0	7
Sand & Silt fractions	7	8.0	8.6	7.1	3.8	nd	4.4	5.1	8.7	5.9
Sand, Silt, & Clay	3	6.7	9.0	5.7	9.0	nd	4.0	13.3	10.0	26.3
Soil pH	3	1.2	0.6	0.2	0.2	1.2	0.4	0.5	0.8	1.5
Cations in NH$_4$CL	4	23.8	18.3	18.5	9.3	13.5	9.3	21.8	14.0	9.7
Cations in NH$_4$OAc	4	12.8	19.8	22.5	5.5	11.3	6.3	15.5	38.9	0.7
Cation Ex. Capacity	2	11.5	16.0	34.5	6.0	4.0	25.5	7.5	19.0	15.0
Exchangeable acidity	3	3.0	4.7	15.3	11.7	32.3	8.7	8.3	5.7	27.7
Cations in CaCl$_2$	6	17.3	17.2	18.2	11.8	44.8	7.5	14.7	15.5	23.0
Extractable Fe and Al	6	6.2	5.8	10.3	5.0	10.0	10.0	6.3	5.8	7.7
Extractable sulfate	2	6.5	2.5	5.5	4.0	5.2	2.5	8.0	2.5	16.5
Sulfate isotherms	6	1.7	2.8	2.7	3.2	4.7	2.7	1.8	3.5	2.5
Total C, N, S	3	19.0	6.3	8.3	12.0	11.3	7.3	16.7	4.7	12.0

[a] Number of parameters included.

[b] Not determined.

quality control audit sample would have known and acceptable analyte concentrations, which the laboratory would be required to duplicate within limits designated on a batch-by-batch basis. The sample would not be blind to the laboratory. If the analytical results were not within designated concentration windows, the batch would be reanalyzed in order to bring the audit sample within tolerance specifications. This would ensure that each laboratory could meet a rigid standard for each batch of samples analyzed prior to final submission of the analytical results. Between-batch error and interlaboratory differences would be reduced. Therefore, *it is further recommended that the laboratories be required to report the analytical results of the analyses on a batch-by-batch basis to the QA staff immediately after the analysis of each batch.*

It was noted that both the precision and the interlaboratory difference estimates were high in some cases. Soil analytical methods which determine extractable (or exchangeable) soil constituents rather than those which determine the total amount present in the soil, are uniquely composed of two main sources of error, extraction error and instrumental error. The former is assumed to be the main cause of differences among the laboratories and is a major reason for conducting interlaboratory analytical survey programs. Without distinguishing between extraction and instrumental error, however, it is not known whether one or both types of errors are present and where to focus efforts to reduce systematic bias. *It is recommended that liquid audit samples be incorporated into the quality assurance program and be used to differentiate between the error sources resulting from extraction and those resulting from instrumentation.*

Quality is a continuum and the need for improved data quality dictates the data quality objective chosen. These DQOs may or may not be attainable with the current technology. Interlaboratory differences for several parameters are relatively high. The analytical procedures within the methods should be examined for their ability to accomplish the analysis at the level specified. If the critical value for relative interlaboratory difference is set at 5 percent, then the results of this survey suggest that only the methods used for the soil pH and sulfate isotherm parameters remain as viable methods. If a level of 10 percent is chosen, several parameter groups still remain a problem (see Table 4-2). *It is recommended that the analytical procedures for specific parameters be reviewed, tested, modified, and clarified, where appropriate.*

It is recommended that the issue of accuracy be addressed since the current approach using interlaboratory differences has limited utility. The use of external laboratories to analyze the audit samples would generate accepted "true" values for comparison among laboratories.

It is recommended that data quality objectives for accuracy be established. In the Northeastern survey, each of the four laboratories exhibited high differences for certain parameters. Serious consideration should be given to either (1) modifying the method or clarifying a procedure within the method, or (2) replacing the method altogether. A case in point for the former is cation exchange capacity and for the latter is the specific surface determination. The Interlaboratory Comparison Study will perhaps provide additional information on DQOs for accuracy for the audit samples.

Representativeness

In evaluating representativeness of the quality assurance samples, some trends can be noted. First, the field duplicates are representative of the range of concentration in the range of the routine samples for most parameters. Second, the preparation duplicates are only rarely representative of the routine samples. Third, the preparation duplicates consistently represent only the extreme lower range of routine sample concentration for a given parameter. A likely explanation for this finding is that the preparation laboratory personnel apparently selected bulk samples for duplication based not on random selection but on the quantity of each sample available. The sampling crews were able to collect the largest amount of sample from the thicker horizons normally found in the lower portion of the soil pedon. An assessment of the horizon types selected for duplication revealed that only 15 of the 55 preparation duplicates (27 percent) were subsamples from Oa, A, E, or strongly illuviated B horizons. Selection appears to have been highly skewed (73 percent) toward the transitional B and the C horizons, which typically have very low analyte concentrations in their extracts.

It is recommended that the laboratory protocols specify a statistically valid method for selecting the preparation duplicate. The method should be reiterated to the laboratory personnel during the pre-sampling training session. The QA field auditor should ensure that a sufficient amount of soil is collected for each bulk sample during sampling to allow a preparation duplicate to be subsampled.

Completeness

Sampling of the specified pedons had a completeness level of 95.9 percent. Processing was accomplished for 100 percent of the pedon samples received by the preparation laboratories.

The analytical completeness level exceeded 99 percent for all parameters. Sufficient data were generated to make conclusions for each parameter in the data bases, with the possible exception of iron in the calcium chloride extract.

Comparability

Sampling, preparation, and analytical methods and protocols for the DDRP Northeastern Soil Survey were comparable and nearly identical to those used for the DDRP Southern Blue Ridge Province Survey. As described in Section 3, the data user is cautioned that some of the field duplicate data may not be comparable for certain applications.

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Appendix A

Verification Flags Used in the Northeastern Soil Survey Data Bases

The following table presents the data verification flags used to identify anomalous data points during the verification of data collected for the DDRP Northeastern Soil Survey.

Appendix A. Table of Flags Used in the Northeastern Soil Survey

Reagent/Calibration Blanks

B3	Reagent Blank > 2 times the CRDL (reagent blank flag)
B4	Blank value is negative
B5	Reagent Blank > CRDL
B6	Calibration Blank > CRDL
B7	Calibration Blank > 1.05 times the Reagent Blank
B8+	SP_SUR: Calibration Blank > 1 milligram
W1	Reagent Blank ≥ 0.5 times the sample value (sample < 2 times the Reagent Blank)
W2+	pH measurements: Reagent Blank < 6 or > 7

Quality Control Check Samples

Q1	QCCS was above contractual criteria
Q2	QCCS was below contractual criteria
Q3	Insufficient number of QCCS measured
Q4	Theoretical DL-QCCS > 3 times the CRDL
Q5+	Measured DL-QCCS was not within 20% of theoretical value
Q6+	Measured and theoretical DL_QCCS is negative

Duplicate

F1	Field duplicate precision > 10% RSD and both routine and duplicate values > 10 times the CRDL
F2	Field duplicate pH precision > 10% RSD
F3	Field duplicate particle size precision > 10% RSD and both routine and duplicate values > 5.0 wt%
P1	Preparation duplicate precision > 10% RSD and both routine and duplicate sample concentrations > 10 times the CRDL
P2	Preparation duplicate pH precision > 10% RSD
P3	Preparation duplicate particle size precision > 10% RSD and both routine and duplicate values > 5.0 wt%
A1	Audit duplicate > 10% RSD and both audit pair concentrations > 10 times the CRDL
A2	Audit sample pH precision > 10% RSD
A3	Audit sample particle size precision > 10% RSD and both routine and duplicate values > 5.0 wt%
D1	Analytical duplicate precision > 10% RSD and both the routine and duplicate samples > 10 times the CRDL
D2	Analytical duplicate pH precision > 10% RSD
D3	Analytical duplicate particle size precision > 10% RSD and both routine and duplicate values > 5.0 wt%

Matrix Spike

S1	Percent recovery of matrix spike was above (> 115%) contractual criteria
S2	Percent recovery of matrix spike was below (< 85%) contractual criteria

Instrumental Detection Limit

L1	IDL > CRDL

Sulfur Relation Determination

K0	Parameter out of range; C_TOT > 60% and S_TOT > 0.5%
K1	Organic soil and $\mathrm{SO_4\_H_2O} > 1.05 \times \mathrm{SO_4\_PO_4}$ (only if both are > 5 mg/kg): both values flagged
K2	Mineral soil and $\mathrm{SO_4\_H_2O} > 1.05 \times \mathrm{SO_4\_PO_4}$ (only if both are > 5 mg/kg): both values flagged
K5	Organic: $\mathrm{SO_4\_H_2O}$ or $\mathrm{SO_4\_PO_4}$ not in range 0 to 100 mg/kg; Mineral: $\mathrm{SO_4\_PO_4}$ or $\mathrm{SO_4\_H_2O}$ not in range 0-250 mg/kg
K6	Organic sample doesn't meet following criteria for sulfate (mg s/L): $\mathrm{SO_4\_0} = 0$ to 20, $\mathrm{SO_4\_2} \geq 22$, $\mathrm{SO_4\_4} \geq 24$, $\mathrm{SO_4\_8} \geq 28$, $\mathrm{SO_4\_16} \geq 36$, $\mathrm{SO_4\_32} \geq 52$ or Sample doesn't fall within following relationship: $\mathrm{SO_4\_0} < \mathrm{SO_4\_2} < \mathrm{SO_4\_4} < \mathrm{SO_4\_8} < \mathrm{SO_4\_16} < \mathrm{SO_4\_32}$ (organic and mineral)
K7	Ratio of $\mathrm{SO_4\_H_2O}:\mathrm{SO_4\_0}$ flagged when ratio is < 5 or > 25

Iron/Aluminum Determination

M1	Flag if AL_KCL ≤ AL_CL2

Miscellaneous

A0*	Value missing
X0*	Invalid but confirmed data based on QA/QC data review

(continued)

Appendix A. (continued)

Miscellaneous (continued)

X1*+	Invalid but confirmed data; potential gross contamination of sample
X2*	Invalid but confirmed data; potential sample switch
X3+	Possible contamination due to either sampling techniques, e.g., bucket augering, or soil amendments, e.g., herbicides, liming, manure, etc.
X4*	Outliers due to internal consistency check; data checked only for transcription errors

Laboratory Tags

CC	Soil retrieved from disqualified analytical laboratory
JJ	Insufficient soil for analysis/reanalysis
RR	Reanalyzed
UU	Unnecessary for parameter
XX	No sample (initiated at preparation laboratory)

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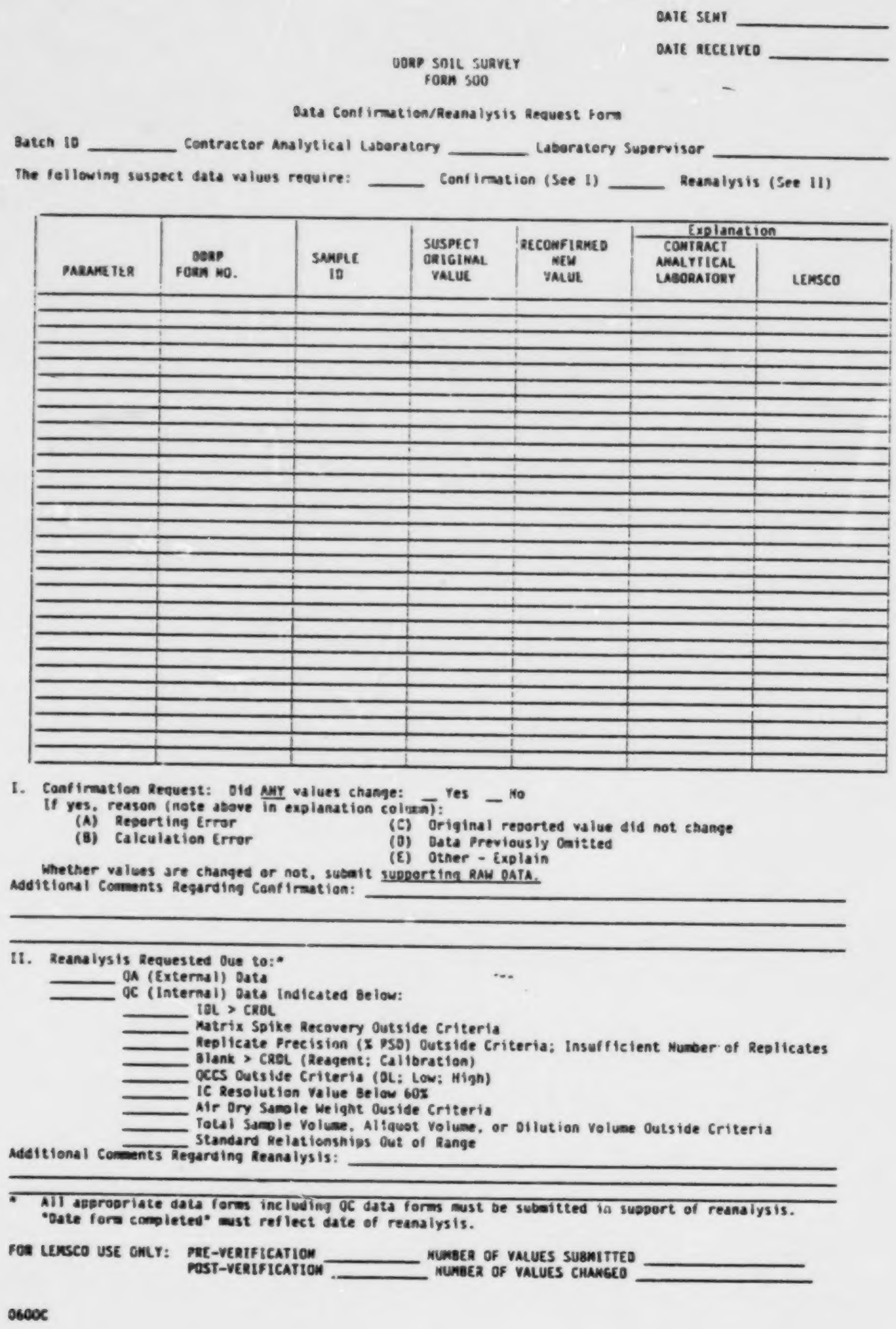
* Sample flag - paramter flagged only for affected samples
+ New flag - not on list of flags distributed 7/87

Appendix B

Data Verification Worksheets and Tables

Data verification was accomplished using the DDRP Quality Assurance Plan (Bartz et al., 1987) as a guide. Figures B-1 and B-2 from that document serve as examples of some of the prominent quality assurance worksheets used during data verification. Also provided is the Data Verification Template in Figures B-3 through B-13. The template was used to guide the quality assurance staff through complex procedures used to verify the data. The template was developed by the Soils Quality Assurance Section of Lockheed Engineering & Sciences Company, Las Vegas, Nevada.

The latter portion of Appendix B includes data from some of the primary verification activities. Tables B-1 and B-2 provide information on the quality control check sample compliance and the internal consistency checks.



DATE SENT ______________

DATE RECEIVED ______________

DDRP SOIL SURVEY
FORM 500

Data Confirmation/Reanalysis Request Form

Batch ID __________ Contractor Analytical Laboratory __________ Laboratory Supervisor ______________

The following suspect data values require: ______ Confirmation (See I) ______ Reanalysis (See II)

PARAMETER	DDRP FORM NO.	SAMPLE ID	SUSPECT ORIGINAL VALUE	RECONFIRMED NEW VALUE	Explanation	
					CONTRACT ANALYTICAL LABORATORY	LEMSCO

I. Confirmation Request: Did ANY values change: __ Yes __ No
If yes, reason (note above in explanation column):
(A) Reporting Error
(B) Calculation Error
(C) Original reported value did not change
(D) Data Previously Omitted
(E) Other - Explain

Whether values are changed or not, submit supporting RAW DATA.
Additional Comments Regarding Confirmation: ______________________________

II. Reanalysis Requested Due to:*
________ QA (External) Data
________ QC (Internal) Data Indicated Below:
    ________ IDL > CRDL
    ________ Matrix Spike Recovery Outside Criteria
    ________ Replicate Precision (% PSD) Outside Criteria; Insufficient Number of Replicates
    ________ Blank > CRDL (Reagent; Calibration)
    ________ QCCS Outside Criteria (DL; Low; High)
    ________ IC Resolution Value Below 60%
    ________ Air Dry Sample Weight Ouside Criteria
    ________ Total Sample Volume, Aliquot Volume, or Dilution Volume Outside Criteria
    ________ Standard Relationships Out of Range

Additional Comments Regarding Reanalysis: ______________________________

* All appropriate data forms including QC data forms must be submitted in support of reanalysis. "Date form completed" must reflect date of reanalysis.

FOR LEMSCO USE ONLY: PRE-VERIFICATION __________ NUMBER OF VALUES SUBMITTED ______________
POST-VERIFICATION __________ NUMBER OF VALUES CHANGED ______________

0600C

Figure B-1. DDRP Form 500 (Data Confirmation/Reanalysis Request).

I. OUTSTANDING ISSUES - CONTRACTOR ANALYTICAL LABORATORY

The following items that are identified as missing should be resubmitted and problems should be resolved before verification is completed:

A. General (forms 102-108)
  1. Required forms have been submitted.
  2. Laboratory name, batch ID, preparation laboratory name, laboratory manager's signature, date for completed, and date batch received are included on all forms.
  3. Correct data qualifiers (tags) were used as needed (see Table 1).

B. Data examination (forms 103-108)
  1. Check that audit pairs are within established control criteria.
  2. Estimate %RSD for all paired QA samples for each parameter, and record in Table 3.
  3. Check the internal consistency of the data.
    a. Form 103a: pH: $H_2O > 0.002M\ CaCl_2 > 0.01M\ CaCl_2$
    b. Form 103b: sand + silt + clay = 100 ± 0.2.
    c. Form 104d: CEC NH_4OAc > CEC NH_4Cl.
    d. Form 106: Extractable Sulfate: $H_2O < PO_4$.
    e. Form 106: Exchangeable Acidity: $BaCl_2 > KCl$.
    f. Form 107: Sulfate Isotherms: $0 < 2 < 4 < 8 < 16 < 32$ mg S/L.
    g. Form 104c: Extraction ratio is 1:2 for mineral samples and 1:10 or 1:25 for organic samples.
    h. Form 103b and 108: For particle size analysis and specific surface, organic samples are reported as a U.

C. General (forms 109-116)
  1. Required forms have been submitted.
  2. Laboratory name, batch ID, and laboratory manager's signature are included on all forms.

D. Data examination (forms 109-116)
  1. Forms 109a-c: Detection limits
    a. Check that instrumental detection limits (IDL) and associated dates of determination are tabulated. IDL should be updated monthly for each parameter.
    b. IDL should be less than or equal to the contract-required detection limit (CRDL) for each parameter.
  2. Form 110a-c: Matrix Spikes
    a. Identify samples used for spiking.
    b. Check that percent recovery for matrix spikes is reported for each parameter required.
    c. Check that percent recovery is calculated correctly (recalculated at least three per page).
    d. Check that percent recovery is 100 ± 15% for each parameter; if it is not, then spiking must be repeated on two different samples.
    e. Verify that the level of spike is 10 times the CRDL or equal to the endogenous level, whichever is greater.
    f. Check that the sample used for Total S, N, and C is not an organic sample for each batch.
  3. Form 111a-i: Replicates
    a. Replicate precision results are reported for each parameter. For pH and specific surface, triplicates are determined.
    b. Correct equation is used to calculate %RSD (degree of freedom equal n-1).
    c. %RSDs are 0-10% (except on fractionated sand and silt).

Figure B-2. Data Completeness Checksheet (1 of 2)

4. Forms 112a-h: Blanks and QCCS
    a. Calibration blanks, reagent blanks, and detection limit (DL) QCCS are reported where required.
    b. Calibration and reagent blanks should be less than or equal to the CRDL.
    c. Forms 112g: K-factors are reported correctly.
    d. Forms 112h: Three high EGME blanks are reported correctly.
    e. DL QCCS theoretical values are approximately 2 to 3 times the CRDL, and the measured values are within 20% of the theoretical value.
    f. QCCS true values are approximately in the midrange of the reported sample values or of the calibration curve.
    g. Initial, continuing, and final QCCS values are within upper and lower control limits.
5. Form 113: Ion Chromatography
    a. IC resolution test results are reported.
    b. Resolution value exceeds 60%.
    c. Peaks are clean on chromatogram(s).
    d. At least one chromatogram is provided for each day of operation for each instrument.
6. Form 114: Standard Additions
    a. Standard additions are performed and results are reported when matrix spike results do not meet contractual requirements.
7. Forms 115a-e: Air-dried Sample Weights
    a. The air-dried soil weight is reported for each parameter, except for particle size analysis (oven dried) and specific surface (P_2O_5 wt. = oven dried).
    b. Weights are reported correctly (see Table 2).
    c. Form 115a: One sample is determined in triplicate for moisture and specific surface.
    d. Duplicates are reported correctly.
8. Forms 116a-h: Dilution Factors
    a. Total sample volume, aliquot volume, total dilution volume, dilution concentrations, and dilution blanks are recorded for each sample.

E. Forms 200: Blank-corrected data
1. Required forms 204-208 have been submitted.
2. Laboratory name, batch ID, preparation laboratory name, manager's signature, and date batch received are included on all forms.
3. Correct number of samples were analyzed, and the results for each parameter are tabulated.

F. Forms 300: Raw Data
1. Required forms 303b-308 have been submitted.
2. Laboratory name, batch ID, preparation laboratory name, laboratory manager's signature, and date batch received are included on all forms.
3. Correct number of samples were analyzed, and the results for each parameter are tabulated.

G. Reporting units are correct on the following forms (see Table 4):
1. 103-108
2. 109: Detection limits
3. 110: Matrix Spikes
4. 111: Replicates
5. 112: Blanks and QCCS
6. 115: Air Dry Sample Weights
7. 116: Dilution Factors/Concentration
8. 200: Blank-Corrected Data
9. 300: Raw Data

Figure B-2. Data Completeness Checksheet (2 of 2)

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs. conc.	Either value greater than 1.2 x or less than 0.8 x None	Both within windows. %RSD in on praph of %RSD vs conc.
Prep	%RSD out on graph of %RSD vs. conc.	None	%RSD in on graph of %RSD vs. conc.
Field	None	%RSD out on graph of %RSD vs. conc.	%RSD in on graph of %RSD vs. conc.
Internal Replicates (3 reps)	None	%RSD > 10.0%	%RSD < 10.0%
Blanks	None Effects > 25% of values (Effects=blanks constites 20% of sample conc.)	Not using 3 high EGME blanks (some contracts required low, med, high blanks) EGME blanks did not equil. at < 1 mg	Used 3 high EGME blanks which equil. at < 1 mg.
DL QCCS	NA	NA	NA
QCCS	Initial, final, or continuing QCCS above or below absolute contract limit or lab's 95%, whichever is greater	True QCCS not in mid-calibration range Marked change from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calibration range No significant change w/i QCCS values
Matrix spike	NA	NA	NA
Standard Relationship	None	None	None
IDL > CRDL	NA	NA	NA

Figure B-3. Quality Assurance Reanalysis Template for Specific Surface.

	Major	Minor	Non
Audits	Either value out of window Sand, silt, or clay: %RSD out on graph of %RSD vs. conc.	Either value greater than 1.2 mean or less than 0.8 mean Sand or silt fractions: %RSD out on graph of %RSD vs. conc.	Both within windows. %RSD in on graph of %RSD vs. conc.
Prep	Sand, silt, or clay: %RSD out on graph of %RSD vs. conc.	Sand or silt fractions: %RSD out on graph of %RSD vs. conc.	%RSD in on graph of %RSD vs. conc.
Field	None	Sand, silt, or clay: %RSD out on graph of %RSD vs. conc.	%RSD in on graph of %RSD vs. conc.
Internal Replicates	%RSD greater than 10.0% and both values greater than 5%	%RSD greater than 10.0% and one value greater than 5%	%RSD greater than 10.0% and no values greater than 5%, or %RSD less than 10.0%
Blanks	None	Clay blank not approx. 0.01	Clay blank approx. 0.01
DL QCCS	NA	NA	NA
QCCS	Initial, final, or continuing QCCS above or below absolute contract limit, or lab's 95%, whichever is greater	True QCCS not in mid-calibration range Marked change from one QCCS to another of 5% or any diff. w/i batch QCCS of 10%	True QCCS within calibration range No significant change w/i QCCS values
Matrix spike	NA	NA	NA
Standard Relationship	None	Sand + silt + clay > 100% ±0.1% Sand fraction not equal to sand Silt fractions not equal to silt	Sand + silt + clay = 100% ±0.1% Sand fractions = sand Silt fractions = silt
IDL > CRDL	NA	NA	NA

Figure B-4. Quality Assurance Reanalysis Template for Particle Size Analysis.

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD > to 0%	%RSD in on graph of %RSD vs Conc.
Internal Replicates	Triplicates not within 0.1 pH units	None	Triplicate within 0.1 pH units
Blanks	None	None	Reagent blank is solution added to the soil
DL QCCS	NA	NA	NA
QCCS	Initial, Final, or Cont. QCCS not within 0.1 pH units of true QCCS	Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCSs of 10%	Init. Cont. and Final QCCS w/in 0.1 pH units of true QCCS, and no sign, chg. between QCCS values
Matrix Spikes	NA	NA	NA
Standard Relationships	None	pH_H20 < pH_002 CaC12 < pH_01 CaC12	pH_H20 > pH_002 CaC12>pH_01 CaC12
IDL > CRDL	NA	NA	NA

Figure B-5. Quality Assurance Reanalysis Template for pH.

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of %RSD vs Conc.
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD out on graph of %RSD vs Conc.	%RSD in on graph of %RSD vs Conc.
Internal Replicates	%RSD > 10.0% Both values > 10 x CRDL	%RSD > 10.0% One value > 10 x CRDL	%RSD > 10.0%; no values > 10 x CRDL; %RSD < 10.0%
Blanks	Blank > Contract Require Effects > 25% of values (Effects=blank constitutes 20% of sample conc.)	Blank > Contract Require Effects 0-25% of values	Blank > Contract Require Effects 0% of values Blank < Contract Require
DL QCCS	None	DL QCCS, theo. not 2-3 x CRDL or IDL, where applicable DL QCCS, meas. not 20% theo.	DL QCCS, theo. 2-3 x CRDL DL QCCS meas. 20% theo.
QCCS	Initial, Final, or Cont. QCCS above or below absolute contract limit or lab's 95%, whichever >	True QCCS not mid calib. range Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calib. range No sign. chg. w/in QCCS values
Matrix Spikes	%Recovery > 100 + or - 15.0%	Spike added not 50-200% of the endogenous level	%Recovery 100 + or - 15.0% Spike added 50-200% of endogenous level
Standard Relationships	None	Ca < Mg < K < Na	Ca > Mg > K > Na
IDL > CRDL	IDL > CRDL and Effects 25% of values (Effects=CRDL constitutes 20% of sample conc.)	IDL > CRDL and Effects 0-25% of values	IDL > CRDL and Effects 0% of values IDL = CRDL IDL < CRDL

Figure B-6. Quality Assurance Reanalysis Template for Exchangeable Cations.

	Major	Minor	None
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of %RSD vs Conc.
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD out on graph of %RSD vs Conc.	%RSD in on graph of %RSD vs Conc.
Internal Replicates	%RSD > 10.0% Both values > 10 x CRDL	%RSD > 10.0% One value > 10 x CRDL	%RSD > 10.0%; no values > 10 x CRDL %RSD < 10.0%
Blanks	Blank > Contract Require. Effects > 25% of values (Effects=blank constitutes 20% of sample conc.)	Blank > Contract Require. Effects 0-25% of values	Blank > Contract Require Effects 0% of values Blank < Contract Require
DL QCCS (may be NA if titration)	None	DL QCCS, theo. not 2-3 x CRDL or IDL, where applicable DL QCCS, meas. not 20% theo.	DL QCCS, theo. 2-3 X CRDL DL QCCS, meas. 20% theo.
QCCS (may be NA if titration)	Initial, Final, or Cont. QCCS above or below absolute contract limit or lab's 95%, whichever >	True QCCS not mid calib. range Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calib. range No sign. chg. w/in QCCS values
Matrix Spikes	%Recovery > 100 + or - 15.0%	Spike added not 50-200% of the endogenous level	%Recovery 100 + or - 15.0% Spike added 50-200% of endogenous level
Standard Relationships	None	NH_4OAc < NH_4Cl	NH_4OAc > NH_4Cl
IDL > CRDL	IDL > CRDL and Effects 25% or values (Effects=CRDL constitutes 20% of sample conc.)	IDL > CRDL and Effects 0-25% of values	IDL > CRDL and Effects 0% of values IDL = CRDL IDL < CRDL

Figure B-7. Quality Assurance Reanalysis Template for Cation Exchange Capacity.

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of %RSD vs Conc.
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD out on graph of %RSD vs Conc.	%RSD in on graph of %RSD vs Conc.
Internal Replicates	%RSD > 10.0% Both values > 10 X CRDL	%RSD > 10.0% One value > 10 x CRDL	%RSD > 10.0%; no values >10 x CRDL %RSD < 10.0%
Blanks (No Calibration Blanks)	Blank > Contract Require Effects > 25% of values (Effects = blank constitutes 20% of sample conc.)	Blank > Contract Require Effects 0-25% of values	Blank > Contract Require Effects 0% of values Blank < Contract Require
DL QCCS	NA	NA	NA
QCCS	Initial, Final, or Cont. QCCS above or below absolute contract limit or lab's 95%, whichever >	True QCCS not mid calib. range Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calib. range No sign. chg. w/in QCCS values
Matrix Spikes	NA	NA	NA
Standard Relationships	None	BaC12 < KCL	BaC12 > KCl
IDL > CRDL	IDL > CRDL and Effects 25% of values (Effects = CRDL constitutes 20% of sample conc.)	IDL > CRDL and Effects 0-25% of values	IDL > CRDL and Effects 0% of values IDL = CRDL IDL < CRDL

Figure B-8. Quality Assurance Reanalysis Template for Exchangeable Acidities.

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of %RSD vs Conc.
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD out on graph of %RSD vs Conc.	%RSD in on graph of %RSD vs Conc.
Internal Replicates	%RSD > 10.0% Both values > 10 x CRDL	%RSD > 10.0% One value > 10 x CRDL	%RSD > 10.0%; no values > 10 x CRDL %RSD < 10.0%
Blanks	Blank > Contract Require. Effects > 25% of values (Effects=blank constitutes 20% of sample conc.)	Blanks > Contract Require Effects 0-25% of values	Blank > Contract Require Effects 0% of values Blank < Contract Require
DL QCCS	None	DL QCCS, theo. not 2-3 x CRDL or IDL, where applicable DL QCCS, meas. not 20% theo.	DL QCCS, theo. 2-3 x CRDL DL QCCS, meas. 20% theo.
QCCS	Initial, FInal, or Cont. QCCS above or below absolute contract limit or lab's 95%, whichever >	True QCCS not mid calib. range Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calib. range No sign. chg. w/in QCCS values
Matrix Spikes	%Recovery > 100 + or - 15.0%	Spike added not 50-200% of the endogenous level	%Recovery 100 + or - 15.0% Spike added 50-200% of endogenous level
Standard Relationships	None	None	None
IDL > CRDL	IDL > CRDL and Effects 25% of values (Effects=CRDL constitutes 20% of sample conc.)	IDL > CRDL and Effects 0-25% of values	IDL > CRDL and Effects 0% of values IDL = CRDL IDL < CRDL

Figure B-9. Quality Assurance Reanalysis Template for KCl-Extractable Aluminum.

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of %RSD vs Conc.
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD out on graph of %RSD vs Conc.	%RSD in on graph of %RSD vs Conc.
Internal Replicates	%RSD > 10.0% Both values > 10 x CRDL	%RSD > 10.0% One value > 10 x CRDL	%RSD > 10.0%; no values >10 x CRDL %RSD < 10.0%
Blanks	Blank> Contract Require Effects > 25% of values (Effects=blank constitutes 20% of sample conc.)	Blanks > Contract Require Effects 0-25% of values	Blank > Contract Requires Effects 0% of values Blank < Contract Require
DL QCCS	None	DL QCCS, theo. not 2-3 x CRDL or IDL, where applicable DL QCCS, meas. not 20% theo.	DL QCCS, theo. 2-3 x CRDL DL QCCS, meas. 20% theo.
QCCS	Initial, Final, or Cont. QCCS above or below absolute contract limit or lab's 95%, whichever >	True QCCS not mid calib. range Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calib. range No sign. chg. w/in QCCS values
Matrix Spikes	%Recovery > 100 + or - 15.0%	Spike added not 50-200% of the endogenous level	%Recovery 100 + or - 15.0% Spike added 50-200% of endogenous level
Standard Relationships	None	None	None
IDL > CRDL	IDL > CRDL and Effects 25% of value (Effects=CRDL Constitutes 20% of sample conc.)	IDL > CRDL and Effects 0-25% of values	IDL > CRDL and Effects 0% of values IDL = CRDL IDL < CRDL

Figure B-10. Quality Assurance Reanalysis Template for Extractable Iron and Aluminum.

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of %RSD vs Conc.
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD out on graph of %RSD vs Conc.	%RSD in on graph of %RSD vs Conc.
Internal Replicates	%RSD > 10.0% Both values > 10 x CRDL	%RSD > 10.0% One value > 10 x CRDL	%RSD > 10.0%; no values >10 x CRDL %RSD < 10.0%
Blanks	Blank> Contract Require Effects > 25% of values (Effects=blank constitutes 20% of sample conc.)	Blanks > Contract Require Effects 0-25% of values	Blank > Contract Requires Effects 0% of values Blank < Contract Require
DL QCCS	None	DL QCCS, theo. not 2-3 x CRDL or IDL, where applicable DL QCCS, meas. not 20% theo.	DL QCCS, theo. 2-3 x CRDL DL QCCS, meas. 20% theo.
QCCS	Initial, Final, or Cont. QCCS above or below absolute contract limit or lab's 95%, whichever >	True QCCS not mid calib. range Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calib. range No sign. chg. w/in QCCS values
Matrix Spikes	%Recovery > 100 + or - 15.0%	Spike added not 50-200% of the endogenous level	%Recovery 100 + or - 15.0% Spike added 50-200% of endogenous level
Standard Relationships	None	H2O ext. SO4 > PO4 ext. SO4	H2O ext. SO4 < PO4 ext. SO4
IDL > CRDL	IDL > CRDL and Effects 25% of value (Effects=CRDL Constitutes 20% of sample conc.)	IDL > CRDL and Effects 0-25% of values	IDL > CRDL and Effects 0% of values IDL = CRDL IDL < CRDL

Figure B-11. Quality Assurance Reanalysis Template for Water-Extractable Sulfate and Phosphate-Extractable Sulfate.

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of %RSD vs Conc.
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD out on graph of %RSD vs Conc.	%RSD in on graph of %RSD vs Conc.
Internal Replicates	%RSD > 10.0% Both values > 10 x CRDL	%RSD > 10.0% One value > 10 x CRDL	%RSD > 10.0% ;no values >10 x CRDL %RSD < 10.0%
Blanks	Blank> Contract Require Effects > 25% of values (Effects=blank constitutes 20% of sample conc.)	Blanks > Contract Require Effects 0-25% of values	Blank > Contract Requires Effects 0% of values Blank < Contract Require
DL QCCS (0 Isotherm only)	None	DL QCCS, theo. not 2-3 x CRDL or IDL, where applicable DL QCCS, meas. not 20% theo.	DL QCCS, theo. 2-3 x CRDL DL QCCS, meas. 20% theo.
QCCS	Initial, Final, or Cont. QCCS above or below absolute contract limit or lab's 95%, whichever >	True QCCS not mid calib. range Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calib. range No sign. chg. w/in QCCS values
Matrix Spikes	%Recovery > 100 + or - 15.0%	Spike added not 50-200% of the endogenous level	%Recovery 100 + or - 15.0% Spike added 50-200% of endogenous level
Standard Relationships	None	0 < 2 < 4 < 8 < 16 < 32	0 > 2 > 4 > 8 > 16 > 32
IDL > CRDL	IDL > CRDL and Effects 25% of value (Effects=CRDL Constitutes 20% of sample conc.)	IDL > CRDL and Effects 0-25% of values	IDL > CRDL and Effects 0% of values IDL = CRDL IDL < CRDL
Ion Chromatograph	None	%Resolutions < 60% Chromatographs not clean	%Resolution > 60%; Chromatographs Clean

Figure B-12. Quality Assurance Reanalysis Template for Sulfate Isotherms.

	Major	Minor	Non
Audits	Either value out of window %RSD out on graph of %RSD vs Conc.	Either value greater than 1.2 mean or less than 0.8 mean None	Both within Windows %RSD in on graph of %RSD vs Conc.
Prep	%RSD out on graph of %RSD vs Conc.	None	%RSD in on graph of %RSD vs Conc.
Field	None	%RSD out on graph of %RSD vs Conc.	%RSD in on graph of %RSD vs Conc.
Internal Replicates	%RSD > 10.0% Both values > 10 x CRDL	%RSD > 10.0% One value > 10 x CRDL	%RSD > 10.0%; no values >10 x CRDL %RSD < 10.0%
Blanks (some instruments R-blk NA for Total N & C)	Blank> Contract Require Effects > 25% of values (Effects=blank constitutes 20% of sample conc.)	Blanks > Contract Require Effects 0-25% of values	Blank > Contract Requires Effects 0% of values Blank < Contract Require
DL QCCS	None	DL QCCS, theo. not 2-3 x CRDL or IDL, where applicable DL QCCS, meas. not 20% theo.	DL QCCS, theo. 2-3 x CRDL DL QCCS, meas. 20% theo.
QCCS (K-Factors for TotN and TotC)	Initial, Final, or Cont. QCCS above or below absolute contract limit or lab's 95%, whichever >	True QCCS not mid calib. range Marked chg. from one QCCS to another of 5% or any diff. w/in batch QCCS of 10%	True QCCS w/in mid calib. range No sign. chg. w/in QCCS values
Matrix Spikes	%Recovery > 100 + or - 15.0%	Spike added not 50-200% of the endogenous level	%Recovery 100 + or - 15.0% Spike added 50-200% of endogenous level
Standard Relationships	None	None	None
IDL > CRDL	IDL > CRDL and Effects 25% of value (Effects=CRDL Constitutes 20% of sample conc.)	IDL > CRDL and Effects 0-25% of values	IDL > CRDL and Effects 0% of values IDL = CRDL IDL < CRDL

Figure B-13. Quality Assurance Reanalysis Template for Total Sulfur, Nitrogen, and Carbon.

Table B-1. Occurrences of Less-than-Complete Compliance for Measurement of Quality Control Check Samples

Variable	Laboratory	n	Compliance %
SP_SUR	1	83	83.2
SAND	2	57	84.2
VCOS	1	73	26.1
COS	1	73	24.6
MS	1	73	19.2
FS	1	73	37.0
VFS	2	57	73.7
SILT	2	52	82.7
COSI	2	57	47.4
FSI	2	57	65.0
CLAY	2	57	57.9
PH_H2O	1	105	98.7
K_CL	4	76	96.1
NA_CL	1	100	96.0
MG_OAC	2	107	99.1
NA_OAC	2	107	99.1
CEC_CL	4	81	98.8
CEC_OAC	2	102	99.1
AC_BACL	2	105	94.3
CA_CL2	1	100	98.0
K_CL2	1	100	95.0
NA_CL2	1	101	92.1
FE_CL2	4	78	98.8
AL_CL2	2	108	99.1
FE_PYP	1	100	94.0
AL_PYP	2	106	99.1
FE_AO	4	101	99.1
AL_AO	1	100	99.0
AL_CD	2	106	94.4
SO4_H2O	1	100	95.0
C_TOT	3	23	83.0
N_TOT	1	105	96.2
S_TOT	2	98	99.0

Table B-2. Internal Consistency Checks Performed for the DDRP Northeastern Analytical Verified Data Base

Parameter[a]	Correlations[b]	Data set[c]	r^2 value	
			1st check	2nd check
MOIST	+/-	A	x[d]	x
SP_SUR	+/-	A	x	x
SAND	+/-, FSI	A	.95	.95
VCOS	+/-, COS	A	.62	.62
COS	+/-, MS	A	.74	.74
MS	+/-, COS	A	.74	.74
FS	+/-, SAND	A	.67	.67
VFS	+/-, SAND	A	x	x
SILT	+/-, SAND	A	.96	.96
COSI	+/-, SILT	A	.80	.80
FSI	+/-, SILT	A	.95	.95
PH_H2O	PH_01M	A	.95	.96
PH_002M	PH_01M	A	.98	.98
CA_CL	CA_OAC	A	.94	.96
MG_CL	MG_OAC	A	.82	.83
K_CL	K_OAC	A	.92	.92
NA_CL	NA_OAC	A	.70	.90
CEC_CL	CEC_OAC	A	.99	.89
AC_KCL	AL_KCL	A	.81	.83
AC_BACL	C_TOT	A	.92	.92
CA_CL2	+/-	A	x	x
MG_CL2	+/-	A	x	x
K_CL2	+/-	A	x	x
NA_CL2	+/-	A	x	x
FE_CL2	+/-	A	x	x
AL_CL2	+/-	A	x	x
FE_PYP	FE_AO	A	.91	.90
AL_PYP	AL_CD	A	.89	.89
AL_AO	AL_CD	A	.86	.76
FE_CD	FE_AO	A	.75	.76
SO4_PO4	SO4_H20	A	.50	.50
SO4_0	SO4_H2O	O/M	.93/.88	.94/.80
SO4_2	SO4_H2O	O/M	.97/.86	.97/.68
SO4_4	SO4_H2O	O/M	.96/.82	.96/.51
SO4_8	SO4_H2O	O/M	.96/.76	.96/.29
SO4_16	SO4_H2O	O/M	.89/.62	.90/.07
SO4_32	SO4_H2O	O/M	.89/.10	.89/.72
C_TOT	N_TOT	A	.95	.95
S_TOT	N_TOT	O/M	.25/.76	.36/.66

[a] A variable can be used for more than one correlation, not all variables were used in the correlations

[b] +/- = Outlier check on the highest and lowest 1% of the values

[c] Routine samples used in correlation: A = All samples; O = Organic horizons only; M = Mineral horizons only

[d] x = r^2 not applicable

Appendix C

Statistics for Step Function Precision Estimates

This table provides statistical information that supplements the precision results and discussion found in Section 3. Provided are data relating to the development of delta values, including the standard deviations and proportions. These data can be used to assess the quality of the routine sample data set on the basis of the quality of the QA sample data sets. The table is sorted by parameter and subsorted by data set.

Appendix C. Table of Statistics for Step Function Precision Estimates

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
MOIST	AS	0.1010	0.0 - 2.5	37	1.31	0.0747	0	0.0	0.1157
			2.5 - 5.0	13	2.69	0.1974	0	0.0	0.1841
			5.0 - 8.0	•[a]	•	•		•	•
			8.0 - inf	•	•	•	•	•	•
	PD	0.3951	0.0 - 2.5	50	0.89	0.1345	0	0.0	
			2.5 - 5.0	5	3.75	1.3496	0	0.0	
			5.0 - 8.0	•	•	•	•	•	
			8.0 - inf	•	•	•	•	•	
	FD	0.3784	0.0 - 2.5	175	1.21	0.2003	0	0.0	
			2.5 - 5.0	44	3.46	0.6424	0	0.0	
			5.0 - 8.0	17	6.02	2.0393	0	0.0	
			8.0 - inf	5	9.69	0.6838	0	0.0	PI[b]
	S/H	1.2729	0.0 - 2.5	817	1.10	0.9842			0.747
			2.5 - 5.0	212	3.54	1.9126			0.204
			5.0 - 8.0	46	5.98	2.9528			0.047
			8.0 - inf	2	8.84	3.8738			0.002
SP_SUR	AS	3.8902	0.0 - 10.0	17	2.64	0.3761	0	0.0	2.2620
			10.0 - 30.0	10	23.08	5.2166	0	0.0	4.1551
			30.0 - 50.0	20	37.16	2.9342	0	0.0	5.4857
			50.0 - 70.0	2	55.38	4.4250	0	0.0	4.8918
			70.0 - inf	1	334.5	13.1373	0	0.0	•
	PD	2.6015	0.0 - 10.0	20	5.79	4.1618	0	0.0	
			10.0 - 30.0	25	17.53	2.7206	0	0.0	
			30.0 - 50.0	9	40.03	1.9184	0	0.0	
			50.0 - 70.0	1	54.47	0.4378	0	0.0	
			70.0 - inf	•	•	•	•	•	
	FD	4.4663	0.0 - 10.0	36	5.59	2.1704	0	0.0	
			10.0 - 30.0	109	18.86	3.7719	0	0.0	
			30.0 - 50.0	51	38.36	5.5048	0	0.0	
			50.0 - 70.0	32	58.40	9.8240	0	0.0	
			70.0 - inf	13	89.52	7.9827	0	0.0	PI
	S/H	17.0396	0.0 - 10.0	207	7.35	5.9415			0.179
			10.0 - 30.0	524	19.42	11.5808			0.479
			30.0 - 50.0	254	39.64	19.7251			0.244
			50.0 - 70.0	73	57.21	23.8554			0.078
			70.0 - inf	18	93.77	187.941			0.020
SAND	AS	1.1285	0.0 - 20.0	•	•	•	•	•	•
			20.0 - 40.0	13	28.10	2.8236	6	46.2	4.1241
			40.0 - 60.0	8	56.79	0.5025	1	12.5	2.5845
			60.0 - 80.0	•	•	•	•	•	•
			80.0 - inf	29	89.57	0.8994	9	31.0	0.9367
	PD	2.2778	0.0 - 20.0	1	3.55	0.2121	0	0.0	
			20.0 - 40.0	7	35.86	0.2928	0	0.0	
			40.0 - 60.0	10	53.68	1.3130	5	50.0	
			60.0 - 80.0	14	72.15	4.2490	6	42.9	
			80.0 - inf	23	89.32	1.8037	3	13.0	
	FD	2.2627	0.0 - 20.0	12	13.23	3.8321	4	33.3	
			20.0 - 40.0	33	33.10	1.4098	12	36.4	
			40.0 - 60.0	80	50.23	2.8661	37	46.2	
			60.0 - 80.0	74	70.73	2.4778	28	37.8	
			80.0 - inf	42	89.29	1.5188	13	31.0	PI
	S/H	12.6342	0.0 - 20.0	6	11.09	3.4231			0.009
			20.0 - 40.0	142	33.60	14.9569			0.139
			40.0 - 60.0	319	50.75	13.9573			0.302
			60.0 - 80.0	380	69.82	12.8520			0.346
			80.0 - inf	228	88.43	9.1273			0.204
VCOS	AS	1.1762	0.0 - 4.0	22	2.19	0.4812	0	0.0	0.2472
			4.0 - 8.0	24	5.74	1.2953	0	0.0	0.8248
			8.0 - 14.0	4	8.50	1.4300	0	0.0	0.4509
			14.0 - inf	•	•	•	•	•	•
	PD	1.0853	0.0 - 4.0	18	2.07	0.5657	0	0.0	
			4.0 - 8.0	19	5.71	0.7927	0	0.0	
			8.0 - 14.0	14	10.98	2.0703	0	0.0	
			14.0 - inf	3	23.25	1.9575	0	0.0	

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
	FD	1.1980	0.0 - 4.0	87	2.19	0.6554	0	0.0	
			4.0 - 8.0	95	5.76	0.9908	0	0.0	
			8.0 - 14.0	43	10.15	1.7056	0	0.0	
			14.0 - inf	15	20.27	3.7794	0	0.0	Pi
	S/H	4.7776	0.0 - 4.0	158	2.54	2.6240			0.178
			4.0 - 8.0	625	6.01	3.7953			0.557
			8.0 - 14.0	249	10.15	6.7423			0.226
			14.0 - inf	44	17.03	17.6887			0.038
COS	AS	1.9147	0.0 - 5.0	21	3.69	0.3192	0	0.0	0.2765
			5.0 - 15.0	10	13.81	2.2134	0	0.0	0.6939
			15.0 - 25.0	19	17.09	1.8743	0	0.0	1.5798
			25.0 - 35.0	•	•	•	•	•	•
			35.0 - inf	•	•	•	•	•	•
	PD	0.9192	0.0 - 5.0	10	2.86	0.2366	0	0.0	
			5.0 - 15.0	30	9.86	0.8594	0	0.0	
			15.0 - 25.0	10	18.89	1.4531	0	0.0	
			25.0 - 35.0	4	28.51	1.9758	0	0.0	
			35.0 - inf	1	45.45	0.3536	0	0.0	
	FD	1.3045	0.0 - 5.0	59	3.13	0.4097	0	0.0	
			5.0 - 15.0	139	9.13	0.8861	0	0.0	
			15.0 - 25.0	29	19.17	3.1449	0	0.0	
			25.0 - 35.0	9	30.03	3.0800	0	0.0	
			35.0 - inf	5	44.16	4.1826	0	0.0	Pi
	S/H	5.7035	0.0 - 5.0	115	3.37	2.9780			0.122
			5.0 - 15.0	727	9.56	4.9948			0.671
			15.0 - 25.0	163	18.08	9.4578			0.146
			25.0 - 35.0	56	26.96	10.1576			0.050
			35.0 - inf	15	38.43	9.1520			0.012
MS	AS	0.6219	0.0 - 5.0	13	3.62	0.3679	0	0.0	0.2505
			5.0 - 10.0	8	8.17	0.2795	0	0.0	0.2939
			10.0 - 20.0	•	•	•	•	•	•
			20.0 - 30.0	17	27.15	0.8808	0	0.0	1.4424
			30.0 - inf	12	32.02	2.0453	0	0.0	1.2899
	PD	1.2900	0.0 - 5.0	6	2.22	0.4435	0	0.0	
			5.0 - 10.0	8	7.47	0.1436	0	0.0	
			10.0 - 20.0	24	14.96	2.2450	0	0.0	
			20.0 - 30.0	8	22.26	0.3897	0	0.0	
			30.0 - inf	9	33.53	2.1529	0	0.0	
	FD	0.9433	0.0 - 5.0	36	3.03	0.4262	0	0.0	
			5.0 - 10.0	69	7.35	0.5237	0	0.0	
			10.0 - 20.0	90	13.96	1.0351	0	0.0	
			20.0 - 30.0	35	23.82	1.6979	0	0.0	
			30.0 - inf	11	33.26	1.0158	0	0.0	Pi
	S/H	5.5396	0.0 - 5.0	70	3.83	4.1241			0.075
			5.0 - 10.0	279	7.56	3.8408			0.267
			10.0 - 20.0	519	14.53	5.5536			0.469
			20.0 - 30.0	148	24.00	8.4230			0.137
			30.0 - inf	60	31.85	8.5126			0.052
FS	AS	1.9160	0.0 - 5.0	12	3.90	0.1814	0	0.0	0.3285
			5.0 - 15.0	1	6.85	2.6163	0	0.0	•
			15.0 - 30.0	24	24.41	1.5903	0	0.0	1.7831
			30.0 - 40.0	13	33.32	2.0125	0	0.0	1.7488
			40.0 - inf	•	•	•	•	•	•
	PD	1.1986	0.0 - 5.0	2	1.90	0.8631	0	0.0	
			5.0 - 15.0	19	10.74	1.0599	0	0.0	
			15.0 - 30.0	27	22.39	1.1537	0	0.0	
			30.0 - 40.0	3	30.82	6.7785	0	0.0	
			40.0 - inf	4	47.10	2.8579	0	0.0	
	FD	1.3304	0.0 - 5.0	20	2.98	0.9373	0	0.0	
			5.0 - 15.0	99	10.55	1.1565	0	0.0	
			15.0 - 30.0	109	20.53	1.4520	0	0.0	
			30.0 - 40.0	8	33.80	0.5208	0	0.0	
			40.0 - inf	5	46.56	1.2985	0	0.0	Pi

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
	S/H	6.9211	0.0 - 5.0	16	3.63	3.6040			0.018
			5.0 - 15.0	345	10.76	5.1703			0.336
			15.0 - 30.0	709	20.09	7.7240			0.631
			30.0 - 40.0	6	34.32	16.8554			0.014
			40.0 - inf	0	40.90	•			•
VFS	AS	1.3947	0.0 - 4.0	•	•	•	•	•	•
			4.0 - 8.0	6	7.36	0.8211	0	0.0	0.5378
			8.0 - 15.0	32	10.43	1.4620	0	0.0	1.4401
			15.0 - 25.0	12	20.52	1.4028	0	0.0	1.2315
			25.0 - 35.0	•	•	•	•	•	•
			35.0 - inf	•	•	•	•	•	•
	PD	1.3837	0.0 - 4.0	5	1.97	0.3619	0	0.0	
			4.0 - 8.0	7	6.26	1.6577	0	0.0	
			8.0 - 15.0	22	12.02	1.6981	0	0.0	
			15.0 - 25.0	14	19.47	0.9049	0	0.0	
			25.0 - 35.0	5	27.69	1.2219	0	0.0	
			35.0 - inf	2	39.65	1.4866	0	0.0	
	FD	1.0515	0.0 - 4.0	14	1.96	0.4379	0	0.0	
			4.0 - 8.0	31	5.99	1.3610	0	0.0	
			8.0 - 15.0	103	11.88	0.7936	0	0.0	
			15.0 - 25.0	82	18.80	1.4233	0	0.0	
			25.0 - 35.0	8	31.11	1.9165	0	0.0	
			35.0 - inf	3	41.27	0.3873	0	0.0	
	S/H	5.7470	0.0 - 4.0	22	2.02	1.4575			PI 0.024
			4.0 - 8.0	69	6.26	6.1239			0.069
			8.0 - 15.0	593	11.73	5.1388			0.550
			15.0 - 25.0	385	17.56	6.6311			0.348
			25.0 - 35.0	7	27.57	19.5405			0.007
			35.0 - inf	0	38.85	•			•
SILT	AS	1.3371	0.0 - 10.0	14	3.98	1.0261	6	42.9	1.2729
			10.0 - 20.0	15	14.86	0.9566	5	33.3	1.0094
			20.0 - 40.0	8	24.61	0.7241	1	12.5	2.3129
			40.0 - 60.0	4	59.02	2.3817	3	75.0	0.7879
			60.0 - inf	9	67.45	2.3339	2	22.2	1.6367
	PD	1.7998	0.0 - 10.0	11	4.59	2.3243	1	9.1	
			10.0 - 20.0	13	14.14	4.5485	2	15.4	
			20.0 - 40.0	21	28.10	1.4990	9	42.9	
			40.0 - 60.0	9	48.44	0.6629	2	22.2	
			60.0 - inf	1	61.80	0.2828	0	0.0	
	FD	2.2242	0.0 - 10.0	23	5.50	1.5526	5	21.7	
			10.0 - 20.0	36	16.33	2.1463	16	44.4	
			20.0 - 40.0	85	30.06	2.3892	32	37.6	
			40.0 - 60.0	87	48.06	2.2670	33	37.9	
			60.0 - inf	10	66.29	1.3649	6	60.0	
	S/H	10.5564	0.0 - 10.0	86	5.91	5.7671			PI 0.078
			10.0 - 20.0	189	14.40	10.0868			0.171
			20.0 - 40.0	459	29.92	11.5855			0.419
			40.0 - 60.0	325	45.67	10.7464			0.313
			60.0 - inf	16	64.11	8.7607			0.019
COSI	AS	0.4919	4.0 - 7.5	14	3.57	0.9249	0	0.0	1.2192
			7.5 - 15.0	23	10.09	0.7499	0	0.0	1.1044
			15.0 - 25.0	1	21.70	0.1414	0	0.0	•
			25.0 - inf	12	31.87	1.9814	0	0.0	3.9668
	PD	1.9153	4.0 - 7.5	15	3.55	1.7719	0	0.0	
			7.5 - 15.0	22	10.96	2.7578	0	0.0	
			15.0 - 25.0	15	18.98	1.3953	0	0.0	
			25.0 - inf	3	28.27	1.7224	0	0.0	
	FD	1.6643	4.0 - 7.5	32	4.07	1.4969	0	0.0	
			7.5 - 15.0	84	11.10	2.0147	0	0.0	
			15.0 - 25.0	102	18.95	1.4684	0	0.0	
			25.0 - inf	23	32.84	1.8779	0	0.0	
	S/H	6.0131	4.0 - 7.5	156	4.87	4.4236			PI 0.143
			7.5 - 15.0	368	11.67	5.7529			0.338
			15.0 - 25.0	542	18.31	6.4618			0.501
			25.0 - inf	10	29.28	11.1385			0.018

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
FSI	AS	0.8232	0.0 - 5.0	25	2.22	0.6782	0	0.0	0.2399
			5.0 - 15.0	8	9.55	1.0506	0	0.0	0.9159
			15.0 - 25.0	4	15.30	0.2062	0	0.0	0.2858
			25.0 - 35.0	11	33.37	1.5622	0	0.0	1.1199
			35.0 - 45.0	2	35.88	1.2010	0	0.0	0.5303
			45.0 - inf	•	•	•	•	•	•
	PD	1.0479	0.0 - 5.0	19	2.96	0.5779	0	0.0	
			5.0 - 15.0	19	9.28	1.2380	0	0.0	
			15.0 - 25.0	9	18.99	1.3522	0	0.0	
			25.0 - 35.0	6	29.01	0.6397	0	0.0	
			35.0 - 45.0	2	39.90	0.0707	0	0.0	
			45.0 - inf	•	•	•	•	•	
	FD	1.2935	0.0 - 5.0	29	2.38	0.5504	0	0.0	
			5.0 - 15.0	81	10.44	1.2066	0	0.0	
			15.0 - 25.0	71	19.87	1.0492	0	0.0	
			25.0 - 35.0	43	30.06	2.3155	0	0.0	
			35.0 - 45.0	11	38.80	1.2325	0	0.0	
			45.0 - inf	6	53.02	4.3414	0	0.0	
	S/H	6.6650	0.0 - 5.0	157	3.01	2.8785			PI 0.136
			5.0 - 15.0	349	10.16	5.9457			0.327
			15.0 - 25.0	355	19.01	7.3515			0.324
			25.0 - 35.0	194	29.97	9.4987			0.186
			35.0 - 45.0	16	39.93	7.8107			0.021
			45.0 - inf	5	52.83	3.2695			0.007
CLAY	AS	0.6613	0.0 - 3.0	29	0.84	0.4812	1	3.4	0.6541
			3.0 - 10.0	13	7.05	0.7990	3	23.1	1.4202
			10.0 - 17.0	•	•	•	•	•	•
			17.0 - 25.0	8	18.60	0.5523	0	0.0	0.7368
			25.0 - inf	•	•	•	•	•	•
	PD	0.5557	0.0 - 3.0	29	1.36	0.5101	2	6.9	
			3.0 - 10.0	16	5.61	0.6581	2	12.5	
			10.0 - 17.0	6	14.00	0.4397	0	0.0	
			17.0 - 25.0	3	21.98	0.7246	1	33.3	
			25.0 - inf	1	43.60	0.0000	0	0.0	
	FD	0.8372	0.0 - 3.0	85	1.74	0.6455	6	7.1	
			3.0 - 10.0	94	5.50	0.8115	11	11.7	
			10.0 - 17.0	35	13.00	0.8197	5	14.3	
			17.0 - 25.0	15	20.25	1.0787	1	6.7	
			25.0 - inf	11	29.00	4.0523	7	63.6	
	S/H	3.7665	0.0 - 3.0	344	1.77	1.3689			PI 0.311
			3.0 - 10.0	456	5.20	3.6344			0.431
			10.0 - 17.0	224	13.25	5.8697			0.206
			17.0 - 25.0	29	19.50	8.0278			0.032
			25.0 - inf	22	30.24	15.0571			0.021
PH_H2O	AS	0.0771	0.0 - 4.2	•	•	•	•	•	•
			4.2 - inf	50	4.88	0.0771	1	2.0	0.1256
	PD	0.1234	0.0 - 4.2	4	3.94	0.0137	0	0.0	
			4.2 - inf	51	5.34	0.1336	4	7.8	
	FD	0.0922	0.0 - 4.2	17	3.91	0.0796	1	5.9	
			4.2 - inf	224	5.08	0.0933	17	7.6	
	S/H	0.4648	0.0 - 4.2	69	3.89	0.3053			PI 0.086
			4.2 - inf	1008	5.17	0.4797			0.914
PH_002M	AS	0.0392	2.0 - inf	50	4.53	0.0392	1	2.0	0.0598
	PD	0.0423	2.0 - inf	54	4.73	0.0423	1	1.8	
	FD	0.0644	2.0 - inf	241	4.58	0.0644	6	2.5	
	S/H	0.3989	2.0 - inf	1076	4.62	0.3989			PI 1.000
PH_01M	AS	0.1422	2.0 - inf	50	4.33	0.1422	4	8.0	0.1250
	PD	0.0315	2.0 - inf	55	4.56	0.0315	0	0.0	
	FD	0.0925	2.0 - inf	241	4.40	0.0925	12	5.0	
	S/H	0.4064	2.0 - inf	1077	4.45	0.4064			PI 1.000
CA_CL	AS	0.0440	0.0 - 0.2	16	0.09	0.0587	3	18.8	0.0209
			0.2 - 8.0	34	0.28	0.0347	6	17.6	0.0390
			8.0 - 24.0	•	•	•	•	•	•
			24.0 - inf	•	•	•	•	•	•

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
	PD	0.3259	0.0 - 0.2	32	0.06	0.0232	3	9.4	
			0.2 - 8.0	22	1.66	0.5226	2	9.1	
			8.0 -24.0	1	8.44	0.0976	0	0.0	
			24.0 - inf	•	•	•	•	•	
	FD	0.2323	0.0 - 0.2	135	0.06	0.0243	22	16.2	
			0.2 - 8.0	97	1.75	0.3488	20	20.6	
			8.0 -24.0	6	15.93	1.1664	1	16.7	
			24.0 - inf	•	•	•	•	•	
	S/H	1.3671	0.0 - 0.2	417	0.09	0.1477			PI 0.385
			0.2 - 8.0	652	1.47	1.9948			0.605
			8.0 -24.0	7	10.33	10.0644			0.010
			24.0 - inf	•	•	•			•
MG_CL	AS	0.0127	0.0 - 0.2	41	0.05	0.0086	0	0.0	0.0125
			0.2 - 1.0	8	0.22	0.0227	1	12.5	0.0110
			1.0 - 5.0	•	•	•	•	•	•
			5.0 - inf	•	•	•	•	•	•
	PD	0.0329	0.0 - 0.2	37	0.04	0.0062	0	0.0	
			0.2 - 1.0	12	0.54	0.0695	2	16.7	
			1.0 - 5.0	2	1.79	0.1706	0	0.0	
			5.0 - inf	1	7.51	0.2206	0	0.0	
	FD	0.0626	0.0 - 0.2	174	0.04	0.0120	7	4.0	
			0.2 - 1.0	42	0.48	0.1324	6	14.3	
			1.0 - 5.0	10	2.29	0.3679	1	10.0	
			5.0 - inf	•	•	•	•	•	
	S/H	0.3812	0.0 - 0.2	730	0.05	0.0684			PI 0.667
			0.2 - 1.0	292	0.42	0.4829			0.274
			1.0 - 5.0	46	2.37	2.2757			0.048
			5.0 - inf	7	5.96	15.5759			0.006
K_CL	AS	0.0068	0.0 - 0.2	42	0.04	0.0066	0	0.0	0.0117
			0.2 - 0.4	8	0.24	0.0109	0	0.0	0.0187
			0.4 - 0.6	•	•	•	•	•	•
			0.6 - inf	•	•	•	•	•	•
	PD	0.0132	0.0 - 0.2	53	0.05	0.0132	2	3.8	
			0.2 - 0.4	1	0.23	0.0113	0	0.0	
			0.4 - 0.6	•	•	•	•	•	
			0.6 - inf	•	•	•	•	•	
	FD	0.0144	0.0 - 0.2	223	0.06	0.0114	12	5.4	
			0.2 - 0.4	11	0.29	0.0885	2	18.2	
			0.4 - 0.6	5	0.51	0.0544	1	20.0	
			0.6 - inf	•	•	•	•	•	
	S/H	0.0578	0.0 - 0.2	1044	0.07	0.0513			PI 0.959
			0.2 - 0.4	29	0.26	0.1544			0.037
			0.4 - 0.6	3	0.52	0.6543			0.004
			0.6 - inf	•	•	•			•
NA_CL	AS	0.0218	0.0 - 0.06	41	0.02	0.0093	0	0.0	0.0080
			0.1 - 0.2	3	0.09	0.0868	2	66.7	0.0166
			0.2 - inf	•	•	•	•	•	•
	PD	0.0147	0.0 - 0.06	44	0.02	0.0120	1	2.3	
			0.1 - 0.2	5	0.10	0.0283	2	40.0	
			0.2 - inf	1	0.32	0.0163	0	0.0	
	FD	0.0203	0.0 - 0.06	189	0.03	0.0121	7	3.7	
			0.1 - 0.2	26	0.10	0.0604	9	34.6	
			0.2 - inf	7	0.26	0.0333	1	14.3	
	S/H	0.0743	0.0 - 0.06	855	0.03	0.0300			PI 0.791
			0.1 - 0.2	161	0.08	0.1033			0.152
			0.2 - inf	34	0.35	1.1104			0.030
CA_OAC	AS	0.0293	0.0 - 0.2	19	0.10	0.0245	6	31.6	0.0193
			0.2 - 4.0	31	0.25	0.0326	8	25.8	0.0368
			4.0 -10.0	•	•	•	•	•	•
			10.0 - inf	•	•	•	•	•	•
	PD	0.4736	0.0 - 0.2	31	0.07	0.0247	4	12.9	
			0.2 - 4.0	19	1.29	0.7810	7	36.8	
			4.0 -10.0	3	6.19	0.4266	0	0.0	
			10.0 - inf	•	•	•	•	•	

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
	FD	0.2892	0.0 - 0.2	132	0.06	0.0222	14	10.6	
			0.2 - 4.0	86	1.25	0.3258	17	19.8	
			4.0 - 10.0	13	5.68	2.0132	5	38.5	
			10.0 - inf	4	18.36	5.7066	1	25.0	
	S/H	1.1573	0.0 - 0.2	419	0.09	0.1371			PI 0.387
			0.2 - 4.0	624	1.17	1.4104			0.571
			4.0 - 10.0	31	5.54	6.1867			0.036
			10.0 - inf	2	13.79	19.6508			0.004
MG_OAC	AS	0.0154	0.0 - 0.2	42	0.05	0.0105	1	2.4	0.0067
			0.2 - 0.8	7	0.23	0.0280	1	14.3	0.0218
			0.8 - inf	•	•	•	•	•	•
	PD	0.1120	0.0 - 0.2	38	0.04	0.0293	2	5.3	
			0.2 - 0.8	8	0.37	0.0633	1	12.5	
			0.8 - inf	6	2.54	1.5334	1	16.7	
	FD	0.1087	0.0 - 0.2	182	0.04	0.0152	9	4.9	
			0.2 - 0.8	36	0.43	0.0658	5	13.9	
			0.8 - inf	16	2.07	1.6508	3	18.8	
	S/H	0.2684	0.0 - 0.2	744	0.05	0.0685			PI 0.683
			0.2 - 0.8	286	0.38	0.3984			0.265
			0.8 - inf	46	2.35	2.3588			0.049
K_OAC	AS	0.0068	0.0 - 0.2	42	0.04	0.0065	0	0.0	0.0146
			0.2 - 0.5	8	0.25	0.0158	1	12.5	0.0136
			0.5 - inf	•	•	•	•	•	•
	PD	0.0108	0.0 - 0.2	52	0.05	0.0110	2	3.8	
			0.2 - 0.5	1	0.22	0.0035	0	0.0	
			0.5 - inf	•	•	•	•	•	
	FD	0.0140	0.0 - 0.2	219	0.06	0.0118	6	2.7	
			0.2 - 0.5	15	0.33	0.0691	3	20.0	
			0.5 - inf	3	0.63	0.0459	0	0.0	
	S/H	0.0624	0.0 - 0.2	1044	0.06	0.0556			PI 0.959
			0.2 - 0.5	29	0.28	0.1649			0.035
			0.5 - inf	3	0.56	0.7270			0.004
NA_OAC	AS	0.0133	0.0 - 0.09	41	0.02	0.0132	1	2.4	0.0113
			0.1 - 0.2	2	0.13	0.0171	0	0.0	•
			0.2 - inf	•	•	•	•	•	•
	PD	0.0131	0.0 - 0.09	48	0.03	0.0132	4	8.3	
			0.1 - 0.2	•	•	•	•	•	
			0.2 - inf	1	0.30	0.0064	0	0.0	
	FD	0.0228	0.0 - 0.09	194	0.03	0.0169	10	5.1	
			0.1 - 0.2	14	0.13	0.0238	3	21.4	
			0.2 - inf	11	0.32	0.3332	5	45.5	
	S/H	0.0767	0.0 - 0.09	1024	0.03	0.0492			PI 0.938
			0.1 - 0.2	27	0.14	0.1491			0.027
			0.2 - inf	17	0.50	1.4186			0.018
CEC_CL	AS	0.4380	0.0 - 2.5	14	0.57	0.2223	2	14.3	0.2425
			2.5 - 7.0	14	5.08	0.3885	1	7.1	1.1253
			7.0 - 14.0	22	8.68	0.6974	3	13.6	1.8319
			14.0 - 25.0	•	•	•	•	•	•
			25.0 - inf	•	•	•	•	•	•
	PD	0.8443	0.0 - 2.5	25	1.32	0.4765	5	20.0	
			2.5 - 7.0	22	4.49	0.4224	5	22.7	
			7.0 - 14.0	6	9.40	1.2333	2	33.3	
			14.0 - 25.0	2	15.87	3.3326	1	50.0	
			25.0 - inf	•	•	•	•	•	
	FD	0.8182	0.0 - 2.5	64	1.50	0.2464	12	18.8	
			2.5 - 7.0	88	4.23	0.7177	29	33.0	
			7.0 - 14.0	67	9.55	0.8203	13	19.4	
			14.0 - 25.0	17	17.75	3.7084	5	29.4	
			25.0 - inf	5	29.42	1.5897	1	20.0	
	S/H	3.5307	0.0 - 2.5	276	1.39	1.0380			PI 0.243
			2.5 - 7.0	455	4.57	2.7940			0.413
			7.0 - 14.0	288	9.68	5.5999			0.281
			14.0 - 25.0	57	17.54	8.8351			0.062
			25.0 - inf	0	26.74	•			•

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
CEC_OAC	AS	0.8894	0.0 - 2.5	14	1.00	0.0919	0	0.0	0.2919
			2.5 - 17.0	17	13.22	0.9630	2	11.8	1.8777
			17.0 - 30.0	19	23.42	1.1439	1	5.3	2.4510
			30.0 - inf	•	•	•	•	•	•
	PD	1.6357	0.0 - 2.5	12	1.59	0.4441	4	33.3	
			2.5 - 17.0	38	6.88	1.6460	10	26.3	
			17.0 - 30.0	4	21.31	2.3467	2	50.0	
			30.0 - inf	1	43.01	1.8738	0	0.0	
	FD	2.1539	0.0 - 2.5	30	1.72	0.2772	8	26.7	
			2.5 - 17.0	137	8.26	1.1652	31	22.6	
			17.0 - 30.0	49	22.15	3.5818	13	26.5	
			30.0 - inf	25	41.36	10.2479	3	12.0	Pi
	S/H	7.2981	0.0 - 2.5	119	1.69	1.2758			0.107
			2.5 - 17.0	732	8.28	5.6874			0.669
			17.0 - 30.0	142	23.13	12.0956			0.143
			30.0 - inf	82	37.60	20.0563			0.081
AC_KCL	AS	0.1268	0.0 - 1.0	14	0.17	0.0433	0	0.0	0.0658
			1.0 - 2.5	13	1.62	0.1473	0	0.0	0.1197
			2.5 - 6.0	23	4.21	0.2361	0	0.0	0.5401
			6.0 - inf	•	•	•	•	•	•
	PD	0.2678	0.0 - 1.0	33	0.39	0.0998	0	0.0	
			1.0 - 2.5	9	1.90	0.4701	2	22.2	
			2.5 - 6.0	7	3.19	0.3536	1	14.3	
			6.0 - inf	2	7.32	0.1803	0	0.0	
	FD	0.3995	0.0 - 1.0	91	0.46	0.1619	2	2.2	
			1.0 - 2.5	65	1.73	0.3360	3	4.6	
			2.5 - 6.0	59	3.83	0.4871	3	5.1	
			6.0 - inf	19	8.02	1.9562	2	10.5	Pi
	S/H	1.4963	0.0 - 1.0	465	0.48	0.5931			0.413
			1.0 - 2.5	284	1.64	1.4236			0.255
			2.5 - 6.0	275	3.63	2.5083			0.267
			6.0 - inf	49	7.91	3.5674			0.058
AC_BACL	AS	1.2298	0.0 - 2.5	12	0.88	0.6546	4	33.3	0.6759
			2.5 - 15.0	1	3.05	0.7495	1	100.0	•
			15.0 - 35.0	24	20.00	1.5805	0	0.0	2.1569
			35.0 - inf	12	41.59	3.3816	0	0.0	2.8891
	PD	2.5096	0.0 - 2.5	14	1.72	0.9914	9	64.3	
			2.5 - 15.0	32	7.14	2.6085	14	43.8	
			15.0 - 35.0	7	23.10	2.2113	1	14.3	
			35.0 - inf	1	50.25	3.7477	0	0.0	
	FD	2.6607	0.0 - 2.5	21	1.54	1.2406	11	52.4	
			2.5 - 15.0	111	7.98	2.7100	43	38.7	
			15.0 - 35.0	77	23.55	2.4417	5	6.5	
			35.0 - inf	26	50.49	3.9078	0	0.0	Pi
	S/H	8.4717	0.0 - 2.5	77	1.45	2.2269			0.072
			2.5 - 15.0	630	7.11	5.2532			0.563
			15.0 - 35.0	249	23.33	12.8934			0.250
			35.0 - inf	109	44.18	19.5748			0.104
AL_KCL	AS	0.2042	0.0 - 1.0	13	0.10	0.0353	0	0.0	0.0440
			1.0 - 2.5	16	1.69	0.1403	0	0.0	0.2526
			2.5 - 4.0	13	3.34	0.5928	1	7.7	0.3768
			4.0 - 7.0	7	4.83	0.5847	0	0.0	0.7728
			7.0 - inf	•	•	•	•	•	•
	PD	0.2666	0.0 - 1.0	33	0.30	0.1242	1	3.0	
			1.0 - 2.5	13	1.67	0.4401	1	7.7	
			2.5 - 4.0	2	3.10	0.1093	0	0.0	
			4.0 - 7.0	3	5.36	0.9992	1	33.3	
			7.0 - inf	•	•	•	•	•	
	FD	0.3958	0.0 - 1.0	104	0.36	0.0816	0	0.0	
			1.0 - 2.5	70	1.65	0.6149	6	8.6	
			2.5 - 4.0	35	3.11	0.7294	2	5.7	
			4.0 - 7.0	25	5.18	0.6034	2	8.0	
			7.0 - inf	6	9.48	1.1243	0	0.0	Pi

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
	S/H	1.2795	0.0 - 1.0	527	0.41	0.5012			0.469
			1.0 - 2.5	276	1.62	1.3379			0.257
			2.5 - 4.0	192	3.04	2.3341			0.179
			4.0 - 7.0	62	5.36	2.9541			0.069
			7.0 - inf	18	8.30	3.2465			0.024
CA_CL2	AS	0.0278	0.0 - 0.5	26	0.41	0.0284	10	38.5	0.0501
			0.5 - 1.0	24	0.65	0.0276	5	20.8	0.0769
			1.0 - inf	•	•	•	•	•	•
	PD	0.0354	0.0 - 0.5	15	0.42	0.0257	6	40.0	
			0.5 - 1.0	40	0.65	0.0408	7	17.5	
			1.0 - inf	•	•	•	•	•	
	FD	0.0304	0.0 - 0.5	92	0.39	0.0268	41	44.6	
			0.5 - 1.0	146	0.65	0.0323	32	21.5	
			1.0 - inf	•	•	•	•	•	PI
	S/H	0.1298	0.0 - 0.5	366	0.43	0.1358			0.358
			0.5 - 1.0	706	0.62	0.1193			0.638
			1.0 - inf	4	1.11	1.3697			0.004
MG_CL2	AS	0.0160	0.0 - 0.1	42	0.03	0.0169	23	54.8	0.0135
			0.1 - 0.2	7	0.14	0.0101	1	14.3	0.0110
			0.2 - inf	•	•	•	•	•	•
	PD	0.0179	0.0 - 0.1	40	0.02	0.0196	21	52.5	
			0.1 - 0.2	11	0.13	0.0076	2	18.2	
			0.2 - inf	3	0.25	0.0113	0	0.0	
	FD	0.0083	0.0 - 0.1	194	0.03	0.0053	81	41.6	
			0.1 - 0.2	36	0.14	0.0140	8	22.2	
			0.2 - inf	9	0.26	0.1164	2	22.2	PI
	S/H	0.0454	0.0 - 0.1	941	0.04	0.0399			0.850
			0.1 - 0.2	118	0.14	0.0702			0.129
			0.2 - inf	16	0.23	0.1369			0.016
K_CL2	AS	0.0019	0.0 - 0.05	42	0.01	0.0018	14	33.3	0.0024
			0.1 - 0.1	8	0.06	0.0047	1	12.5	0.0042
			0.1 - inf	•	•	•	•	•	•
	PD	0.0034	0.0 - 0.05	53	0.01	0.0019	25	47.2	
			0.1 - 0.1	1	0.06	0.0068	1	100.0	
			0.1 - inf	1	0.14	0.1846	1	100.0	
	FD	0.0053	0.0 - 0.05	227	0.01	0.0043	**	53.2	
			0.1 - 0.1	10	0.06	0.0090	2	20.0	
			0.1 - inf	3	0.13	0.1334	2	66.7	PI
	S/H	0.0170	0.0 - 0.05	1055	0.01	0.0149			0.969
			0.1 - 0.1	16	0.07	0.0688			0.024
			0.1 - inf	5	0.13	0.1294			0.007
NA_CL2	AS	0.0020	0.0 - 0.05	50	0.02	0.0020	22	44.0	0.0024
			0.1 - 0.1	•	•	•	•	•	•
			0.1 - inf	•	•	•	•	•	•
	PD	0.0072	0.0 - 0.05	52	0.02	0.0069	24	46.2	
			0.1 - 0.1	2	0.07	0.0072	1	50.0	
			0.1 - inf	1	0.16	0.0247	1	100.0	
	FD	0.0077	0.0 - 0.05	219	0.02	0.0068	**	60.6	
			0.1 - 0.1	13	0.07	0.0124	6	46.2	
			0.1 - inf	8	0.16	0.0330	4	50.0	PI
	S/H	0.0245	0.0 - 0.05	961	0.02	0.0137			0.895
			0.05 0.1	99	0.07	0.0974			0.089
			0.1 - inf	16	0.17	0.2246			0.016
AL_CL2	AS	0.0063	0.0 - 0.05	21	0.01	0.0046	11	52.4	0.0070
			0.05- 0.1	8	0.08	0.0085	2	25.0	0.0073
			0.1 - 0.2	13	0.15	0.0143	3	23.1	0.0203
			0.2 - inf	2	0.22	0.0072	0	0.0	0.0088
	PD	0.0079	0.0 - 0.05	33	0.01	0.0054	24	72.7	
			0.05- 0.1	6	0.07	0.0131	2	33.3	
			0.1 - 0.2	4	0.15	0.0140	2	50.0	
			0.2 - inf	2	0.21	0.0182	0	0.0	
	FD	0.0107	0.0 - 0.05	145	0.02	0.0076	**	71.5	
			0.05- 0.1	42	0.07	0.0145	13	31.0	
			0.1 - 0.2	26	0.13	0.0210	13	50.0	
			0.2 - inf	4	0.26	0.0886	2	50.0	PI

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO n	Pairs>DQO %	Between-batch SD
	S/H	0.0425	0.0 - 0.05	717	0.02	0.0300			0.647
			0.05- 0.1	252	0.07	0.0571			0.226
			0.1 - 0.2	51	0.14	0.1082			0.066
			0.2 - inf	2	0.26	0.1111			0.007
FE_CL2	AS	0.0013	0.0 - 0.01	18	0.00	0.0008	10	55.6	0.0025
			0.01- 0.04	13	0.03	0.0029	3	23.1	0.0045
			0.04- inf	9	0.05	0.0055	3	33.3	0.0077
	PD	0.0021	0.0 - 0.01	28	0.00	0.0015	20	71.4	
			0.01- 0.04	3	0.03	0.0045	2	66.7	
			0.04- inf	2	0.08	0.0064	1	50.0	
	FD	0.0032	0.0 - 0.01	143	0.00	0.0016	79	55.2	
			0.01- 0.04	12	0.02	0.0098	5	41.7	
			0.04- inf	6	0.06	0.0164	5	83.3	PI
	S/H	0.0159	0.0 - 0.01	713	0.00	0.0099			0.638
			0.01- 0.04	98	0.02	0.0425			0.098
			0.04- inf	27	0.06	0.0529			0.033
FE_PYP	AS	0.0235	0.0 - 0.2	14	0.04	0.0075	0	0.0	0.0078
			0.2 - 0.33	•	•	•	•	•	•
			0.33- 0.7	26	0.65	0.0571	1	3.8	0.0592
			0.7 - 1.3	10	0.84	0.0312	0	0.0	0.0934
			1.3 - inf	•	•	•	•	•	•
	PD	0.0775	0.0 - 0.2	39	0.06	0.0146	0	0.0	
			0.2 - 0.33	8	0.26	0.0125	0	0.0	
			0.33- 0.7	4	0.53	0.2936	1	25.0	
			0.7 - 1.3	2	0.93	0.0449	0	0.0	
			1.3 - inf	1	1.85	0.0610	0	0.0	
	FD	0.0630	0.0 - 0.2	107	0.08	0.0209	2	1.9	
			0.2 - 0.33	37	0.26	0.0474	4	10.8	
			0.33- 0.7	54	0.48	0.1320	10	18.5	
			0.7 - 1.3	30	0.95	0.0997	5	16.7	
			1.3 - inf	12	2.08	0.2364	4	33.3	PI
	S/H	0.2832	0.0 - 0.2	540	0.08	0.0784			0.484
			0.2 - 0.33	207	0.26	0.2172			0.187
			0.33- 0.7	212	0.53	0.3495			0.212
			0.7 - 1.3	89	0.93	0.8631			0.085
			1.3 - inf	28	2.06	1.7986			0.032
AL_PYP	AS	0.0296	0.0 - 0.2	14	0.06	0.0100	0	0.0	0.0098
			0.2 - 0.33	•	•	•	•	•	•
			0.33- 0.5	2	0.46	0.0302	0	0.0	0.0056
			0.5 - 1.0	33	0.72	0.0562	2	6.1	0.0800
			1.0 - inf	1	1.05	0.0988	0	0.0	•
	PD	0.0286	0.0 - 0.2	36	0.08	0.0190	2	5.6	
			0.2 - 0.33	9	0.26	0.0364	2	22.2	
			0.33- 0.5	3	0.37	0.0149	0	0.0	
			0.5 - 1.0	6	0.70	0.0535	0	0.0	
			1.0 - inf	1	1.42	0.0414	0	0.0	
	FD	0.0513	0.0 - 0.2	81	0.10	0.0186	2	2.5	
			0.2 - 0.33	50	0.27	0.0717	9	18.0	
			0.33- 0.5	42	0.41	0.0376	7	16.7	
			0.5 - 1.0	53	0.73	0.1011	5	9.4	
			1.0 - inf	15	1.59	0.1186	1	6.7	PI
	S/H	0.1918	0.0 - 0.2	450	0.10	0.0712			0.418
			0.2 - 0.33	240	0.26	0.1754			0.214
			0.33- 0.5	171	0.42	0.2348			0.159
			0.5 - 1.0	150	0.71	0.3674			0.149
			1.0 - inf	65	1.20	0.5399			0.060
FE_AO	AS	0.0937	0.0 - 0.2	13	0.06	0.0174	0	0.0	0.0376
			0.2 - 0.33	1	0.20	0.2154	1	100.0	•
			0.33- 0.5	8	0.44	0.0254	0	0.0	0.0486
			0.5 - 1.5	28	1.01	0.1054	4	14.3	0.1946
			1.5 - inf	•	•	•	•	•	•
	PD	0.0619	0.0 - 0.2	26	0.09	0.0122	0	0.0	
			0.2 - 0.33	15	0.27	0.0650	3	20.0	
			0.33- 0.5	7	0.40	0.0718	2	28.6	
			0.5 - 1.5	6	0.98	0.0993	1	16.7	
			1.5 - inf	1	2.42	0.0630	0	0.0	

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO		Between-batch SD
							n	%	
	FD	0.0896	0.0 - 0.2	75	0.10	0.0239	3	4.0	
			0.2 - 0.33	32	0.26	0.0704	7	21.9	
			0.33- 0.5	33	0.43	0.1103	12	36.4	
			0.5 - 1.5	85	0.88	0.1159	10	11.8	
			1.5 - inf	16	2.29	0.3556	4	25.0	
	S/H	0.3795	0.0 - 0.2	304	0.10	0.1107			PI 0.278
			0.2 - 0.33	251	0.27	0.1894			0.225
			0.33- 0.5	152	0.40	0.2729			0.143
			0.5 - 1.5	331	0.86	0.5655			0.312
			1.5 - inf	39	2.28	2.1207			0.043
AL_AO	AS	0.0361	0.0 - 0.2	14	0.08	0.0133	0	0.0	0.0139
			0.2 - 0.33	•	•	•	•	•	•
			0.33- 0.7	8	0.46	0.0335	1	12.5	0.0901
			0.7 - 2.0	28	1.02	0.0820	2	7.1	0.1136
			2.0 - inf	•	•	•	•	•	•
	PD	0.0745	0.0 - 0.2	27	0.11	0.0114	0	0.0	
			0.2 - 0.33	8	0.26	0.0413	1	12.5	
			0.33- 0.7	11	0.50	0.1433	5	45.5	
			0.7 - 2.0	9	1.06	0.0955	1	11.1	
			2.0 - inf	•	•	•	•	•	
	FD	0.2216	0.0 - 0.2	66	0.11	0.0200	3	4.5	
			0.2 - 0.33	36	0.27	0.0260	3	8.3	
			0.33- 0.7	67	0.51	0.0945	13	19.4	
			0.7 - 2.0	57	1.24	0.1919	11	19.3	
			2.0 - inf	15	3.58	2.5963	3	20.0	
	S/H	0.4111	0.0 - 0.2	360	0.12	0.0888			PI 0.333
			0.2 - 0.33	124	0.26	0.1734			0.120
			0.33- 0.7	334	0.48	0.4144			0.307
			0.7 - 2.0	191	1.25	0.7544			0.183
			2.0 - inf	68	2.24	1.6751			0.057
FE_CD	AS	0.0528	0.0 - 0.2	12	0.15	0.0128	0	0.0	0.0170
			0.2 - 0.33	2	0.23	0.0308	0	0.0	0.0227
			0.33- 0.7	2	0.50	0.0166	0	0.0	0.0781
			0.7 - 1.5	20	1.12	0.0827	1	5.0	0.1586
			1.5 - 2.5	14	1.73	0.0564	0	0.0	0.1709
			2.5 - inf	•	•	•	•	•	•
	PD	0.0640	0.0 - 0.2	15	0.12	0.0080	0	0.0	
			0.2 - 0.33	5	0.27	0.0086	0	0.0	
			0.33- 0.7	17	0.51	0.0727	2	11.8	
			0.7 - 1.5	16	1.05	0.0656	2	12.5	
			1.5 - 2.5	2	1.95	0.2173	0	0.0	
			2.5 - inf	•	•	•	•	•	
	FD	0.1496	0.0 - 0.2	37	0.11	0.0342	3	8.1	
			0.2 - 0.33	18	0.27	0.0824	1	5.6	
			0.33- 0.7	65	0.52	0.1113	16	24.4	
			0.7 - 1.5	78	1.07	0.2133	11	14.1	
			1.5 - 2.5	31	1.80	0.1325	2	6.5	
			2.5 - inf	11	3.15	0.2297	1	9.1	
	S/H	0.5436	0.0 - 0.2	125	0.14	0.0916			PI 0.112
			0.2 - 0.33	169	0.25	0.2151			0.155
			0.33- 0.7	171	0.52	0.3653			0.166
			0.7 - 1.5	505	1.04	0.6794			0.456
			1.5 - 2.5	82	1.82	1.0036			0.083
			2.5 - inf	23	3.36	1.7247			0.027
AL_CD	AS	0.0212	0.0 - 0.2	14	0.06	0.0053	0	0.0	0.0126
			0.2 - 0.33	2	0.31	0.0150	0	0.0	0.0011
			0.33- 0.7	19	0.57	0.0276	1	5.3	0.0711
			0.7 - 1.5	15	0.93	0.0675	1	6.7	0.1033
			1.5 - inf	•	•	•	•	•	•
	PD	0.0418	0.0 - 0.2	36	0.10	0.0088	0	0.0	
			0.2 - 0.33	10	0.26	0.0240	0	0.0	
			0.33- 0.7	6	0.46	0.1115	2	33.3	
			0.7 - 1.5	3	1.04	0.0655	0	0.0	
			1.5 - inf	•	•	•	•	•	

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO		Between-batch SD
							n	%	
	FD	0.0582	0.0 - 0.2	81	0.10	0.0164	2	2.5	
			0.2 - 0.33	54	0.27	0.0650	6	11.0	
			0.33- 0.7	63	0.48	0.0686	8	12.7	
			0.7 - 1.5	32	1.10	0.1574	7	21.9	
			1.5 - inf	10	2.14	0.1514	0	0.0	PI
	S/H	0.2432	0.0 - 0.2	499	0.11	0.0749			0.457
			0.2 - 0.33	190	0.28	0.2412			0.175
			0.33- 0.7	211	0.48	0.2752			0.209
			0.7 - 1.5	168	1.10	0.6606			0.151
			1.5 - inf	7	1.86	1.1779			0.008
SO4_H2O	AS	0.8800	0.0 - 5.0	14	2.45	0.5676	0	0.0	0.6198
			5.0 -10.0	11	8.13	0.8753	2	17.4	1.0081
			10.0 -25.0	16	18.60	1.1554	3	18.8	0.9910
			25.0 -40.0	8	32.02	2.2358	2	25.0	2.5001
			40.0 - inf	•	•	•	•	•	•
	PD	3.0805	0.0 - 5.0	27	2.86	0.6874	3	11.1	
			5.0 -10.0	18	7.01	2.0296	4	22.2	
			10.0 -25.0	9	15.48	6.2224	4	44.4	
			25.0 -40.0	1	25.82	26.8474	1	100.0	
			40.0 - inf	•	•	•	•	•	
	FD	1.5978	0.0 - 5.0	66	3.15	0.5883	6	9.1	
			5.0 -10.0	70	7.35	1.1888	20	28.6	
			10.0 -25.0	98	14.44	2.8438	23	23.5	
			25.0 -40.0	4	28.22	1.5561	1	25.0	
			40.0 - inf	3	61.38	35.3671	2	66.7	PI
	S/H	6.0381	0.0 - 5.0	314	3.58	2.0850			0.295
			5.0 -10.0	414	7.40	5.1797			0.377
			10.0 -25.0	345	14.26	10.4484			0.323
			25.0 -40.0	4	25.49	23.7498			0.004
			40.0 - inf	0	126.8	•			•
SO4_PO4	AS	2.9337	0.0 -10.0	14	3.36	0.5110	1	7.1	1.1165
			10.0 -45.0	15	27.33	1.9352	3	20.0	4.6539
			45.0 -90.0	8	76.81	9.4081	2	25.0	5.0968
			90.0 -80.0	13	105.8	2.5433	0	0.0	5.7374
			80.0 - inf	•	•	•	•	•	•
	PD	5.0400	0.0 -10.0	28	5.37	0.7404	5	17.5	
			10.0 -45.0	17	22.11	2.5363	4	23.5	
			45.0 -90.0	6	67.15	17.0740	3	50.0	
			90.0 -80.0	3	116.7	7.2651	0	0.0	
			80.0 - inf	•	•	•	•	•	
	FD	8.4959	0.0 -10.0	66	5.28	1.3653	20	30.3	
			10.0 -45.0	89	26.23	7.3876	30	33.7	
			45.0 -90.0	49	64.43	11.5293	9	18.4	
			90.0 -80.0	25	124.7	17.7788	7	28.0	
			80.0 - inf	9	280.3	36.9148	3	33.3	PI
	S/H	41.5870	0.0 -10.0	248	6.02	6.7118			0.249
			10.0 -45.0	506	24.05	24.6903			0.463
			45.0 -90.0	187	65.50	57.9573			0.170
			90.0 -80.0	95	106.8	100.329			0.084
			80.0 - inf	38	244.9	293.354			0.035
SO4_0	AS	0.0904	0.0 - 1.0	14	0.49	0.0760	8	57.1	0.0788
			1.0 - 3.0	28	1.65	0.1080	16	57.1	0.1659
			3.0 -10.0	8	4.19	0.1986	1	12.5	0.1659
			10.0 - inf	•	•	•	•	•	•
	PD	0.1058	0.0 - 1.0	42	0.51	0.0782	8	19.0	
			1.0 - 3.0	13	1.38	0.1540	5	38.5	
			3.0 -10.0	•	•	•	•	•	
			10.0 - inf	•	•	•	•	•	
	FD	0.1701	0.0 - 1.0	132	0.59	0.0920	50	37.9	
			1.0 - 3.0	105	1.56	0.2838	44	41.9	
			3.0 -10.0	3	4.53	0.4364	1	33.3	
			10.0 - inf	1	13.94	1.1565	1	100.0	PI
	S/H	0.6323	0.0 - 1.0	680	0.64	0.2990			0.619
			1.0 - 3.0	372	1.52	1.0466			0.354
			3.0 -10.0	24	3.64	3.0072			0.025
			10.0 - inf	0	16.49	•			•

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO		Between-batch SD
							n	%	
SO4_2	AS	0.1050	0.0 - 1.0	•	•	•	•	•	•
			1.0 - 4.0	42	2.73	0.1039	5	11.9	0.1612
			4.0 - 10.0	8	5.61	0.1354	1	12.5	0.2678
			10.0 - inf	•	•	•	•	•	•
	PD	0.1955	0.0 - 1.0	•	•	•	•	•	
			1.0 - 4.0	55	2.18	0.1955	11	20.0	
			4.0 - 10.0	•	•	•	•	•	
			10.0 - inf	•	•	•	•	•	
	FD	0.1438	0.0 - 1.0	4	0.80	0.0485	2	50.0	
			1.0 - 4.0	230	2.35	0.1383	67	29.1	
			4.0 - 10.0	6	5.27	0.2489	1	16.7	
			10.0 - inf	1	16.49	1.3217	1	100.0	
	S/H	0.8048	0.0 - 1.0	0	0.93	•			Pi •
			1.0 - 4.0	1045	2.37	0.7330			0.962
			4.0 - 10.0	31	4.98	2.7938			0.035
			10.0 - inf	0	19.66	•			•
SO4_4	AS	0.1807	0.0 - 1.0	•	•	•	•	•	•
			1.0 - 6.0	42	4.17	0.1795	7	16.7	0.2036
			6.0 - 12.0	8	7.02	0.2202	1	12.5	0.3862
			12.0 - inf	•	•	•	•	•	•
	PD	0.2158	0.0 - 1.0	•	•	•	•	•	
			1.0 - 6.0	55	3.73	0.2158	9	16.4	
			6.0 - 12.0	•	•	•	•	•	
			12.0 - inf	•	•	•	•	•	
	FD	0.2941	0.0 - 1.0	•	•	•	•	•	
			1.0 - 6.0	234	3.71	0.1928	48	20.5	
			6.0 - 12.0	6	7.57	3.5183	1	16.7	
			12.0 - inf	1	17.29	2.2188	1	100.0	
	S/H	0.9117	0.0 - 1.0	•	•	•			Pi •
			1.0 - 6.0	1048	3.84	0.8389			0.969
			6.0 - 12.0	28	6.90	3.2955			0.030
			12.0 - inf	0	21.00	•			•
SO4_8	AS	0.2075	0.0 - 1.0	•	•	•	•	•	•
			1.0 - 7.0	14	6.24	0.1062	0	0.0	0.4819
			7.0 - 15.0	36	8.39	0.2845	2	5.6	0.3882
			15.0 - inf	•	•	•	•	•	•
	PD	0.2425	0.0 - 1.0	•	•	•	•	•	
			1.0 - 7.0	23	6.20	0.3162	3	13.0	
			7.0 - 15.0	32	7.70	0.1864	3	9.4	
			15.0 - inf	•	•	•	•	•	
	FD	0.2516	0.0 - 1.0	•	•	•	•	•	
			1.0 - 7.0	114	5.46	0.2343	19	16.7	
			7.0 - 15.0	126	8.01	0.2604	15	11.9	
			15.0 - inf	1	21.15	1.9118	1	100.0	
	S/H	1.2531	0.0 - 1.0	•	•	•			Pi •
			1.0 - 7.0	478	5.90	1.0877			0.432
			7.0 - 15.0	598	8.06	1.3790			0.567
			15.0 - inf	0	24.61	•			•
SO4_16	AS	0.5328	0.0 - 1.0	•	•	•	•	•	•
			1.0 - 13.0	13	11.32	0.3823	1	7.7	0.7778
			13.0 - 25.0	37	15.80	0.6089	4	10.8	0.8274
			25.0 - inf	•	•	•	•	•	•
	PD	0.4509	0.0 - 1.0	•	•	•	•	•	
			1.0 - 13.0	10	11.34	0.6222	2	20.0	
			13.0 - 25.0	45	14.95	0.3642	4	8.9	
			25.0 - inf	•	•	•	•	•	
	FD	0.5639	0.0 - 1.0	•	•	•	•	•	
			1.0 - 13.0	105	10.86	0.6927	21	20.0	
			13.0 - 25.0	135	15.45	0.4943	17	12.6	
			25.0 - inf	1	30.58	2.5963	1	100.0	
	S/H	1.9403	0.0 - 1.0	•	•	•			Pi •
			1.0 - 13.0	374	11.41	2.1652			0.335
			13.0 - 25.0	703	15.34	1.8266			0.663
			25.0 - inf	0	33.76	•			•

continued

Appendix C. Continued

Parameter	Data set	Delta	Window	df	Mean	Within-batch SD	Pairs>DQO		Between-batch SD
							n	%	
SO4_32	AS	0.8419	0.0 - 1.0	•	•	•	•	•	•
			1.0 -20.0	•	•	•	•	•	•
			20.0 -35.0	50	28.57	0.8419	6	12.0	1.2151
			35.0 - inf	•	•	•	•	•	•
	PD	1.5851	0.0 - 1.0	•	•	•	•	•	
			1.0 -20.0	•	•	•	•	•	
			20.0 -35.0	55	29.06	1.5851	6	10.9	
			35.0 - inf	•	•	•	•	•	
	FD	1.0010	0.0 - 1.0	•	•	•	•	•	
			1.0 -20.0	19	17.57	0.5634	2	10.5	
			20.0 -35.0	220	27.95	1.0009	22	10.0	
			35.0 - inf	2	41.34	1.6583	1	50.0	
	S/H	3.0129	0.0 - 1.0	•	•	•			Pi •
			1.0 -20.0	5	18.22	4.3419			0.007
			20.0 -35.0	1071	28.25	3.0023			0.989
			35.0 - inf	1	40.96	3.3810			0.004
C_TOT	AS	0.2087	0.0 - 0.33	14	0.14	0.0224	1	7.1	0.0267
			0.33- 5.0	33	3.04	0.2733	4	12.1	0.2362
			5.0 - 10.0	3	5.96	0.2120	0	0.0	0.2595
			10.0 - 15.0	•	•	•	•	•	•
			15.0 - inf	•	•	•	•	•	•
	PD	0.2323	0.0 - 0.33	28	0.14	0.0244	3	10.7	
			0.33- 5.0	24	1.28	0.2804	5	20.8	
			5.0 - 10.0	3	6.21	0.3716	0	0.0	
			10.0 - 15.0	•	•	•	•	•	
			15.0 - inf	•	•	•	•	•	
	FD	0.4786	0.0 - 0.33	50	0.18	0.0419	3	6.0	
			0.33- 5.0	160	2.05	0.5799	25	15.6	
			5.0 - 10.0	25	6.32	0.4075	1	4.0	
			10.0 - 15.0	3	12.06	8.3238	1	33.3	
			15.0 - inf	3	15.78	1.2893	0	0.0	
	S/H	1.2946	0.0 - 0.33	258	0.16	0.1326			Pi 0.228
			0.33- 5.0	706	1.72	1.2490			0.650
			5.0 - 10.0	110	6.80	3.4967			0.115
			10.0 - 15.0	3	11.92	9.0879			0.005
			15.0 - inf	0	18.90	•			•
N_TOT	AS	0.0091	0.0 - 0.1	10	0.01	0.0033	0	0.0	0.0040
			0.1 - 0.3	35	0.13	0.0233	15	42.9	0.0214
			0.3 - 0.6	•	•	•	•	•	•
			0.6 - inf	•	•	•	•	•	•
	PD	0.0179	0.0 - 0.1	42	0.03	0.0172	9	21.4	
			0.1 - 0.3	4	0.22	0.0095	0	0.0	
			0.3 - 0.6	•	•	•	•	•	
			0.6 - inf	1	0.80	0.9009	1	100.0	
	FD	0.0274	0.0 - 0.1	125	0.04	0.0155	28	22.4	
			0.1 - 0.3	90	0.18	0.0531	36	40.0	
			0.3 - 0.6	13	0.39	0.0227	1	7.7	
			0.6 - inf	5	0.77	0.4338	1	20.0	
	S/H	0.0685	0.0 - 0.1	726	0.04	0.0440			Pi 0.644
			0.1 - 0.3	265	0.18	0.1030			0.262
			0.3 - 0.6	50	0.39	0.1798			0.060
			0.6 - inf	1	0.74	0.0728			0.003
S_TOT	AS	0.0057	0.0 - 0.05	45	0.02	0.0057	4	8.9	0.0050
			0.05- 0.1	•	•	•	•	•	•
			0.1 - inf	•	•	•	•	•	•
	PD	0.0053	0.0 - 0.05	44	0.01	0.0053	2	4.5	
			0.05- 0.1	•	•	•	•	•	
			0.1 - inf	•	•	•	•	•	
	FD	0.0057	0.0 - 0.05	203	0.02	0.0049	7	3.4	
			0.05- 0.1	11	0.07	0.0172	2	18.2	
			0.1 - inf	3	0.18	0.0866	1	33.3	
	S/H	0.0169	0.0 - 0.05	1016	0.02	0.0152			Pi 0.924
			0.05- 0.1	22	0.06	0.0400			0.028
			0.1 - inf	5	0.13	0.1686			0.006

[a] A dot indicates a lack of data within the range of this window.
[b] Pi Proportion of routine samples in the ith window.

Appendix D

Inordinate Data Points Influencing the Precision Estimates

Appendix D provides information on specific data points that have an inordinate effect on the precision estimates presented in the results and discussion of Section 3. Included is information on each parameter for each data set for the sampling class/horizon group, the batch/sample number, and the reason for its effect on the estimates. Data users interested in the quality of data in specific batches will find this table particularly helpful. The table is sorted by parameter and subsorted by data set.

Appendix D. Inordinate Data Points Having a High Degree of Influence on the Precision Estimates for the Data Sets

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
MOIST	S/H	I05 / Oe		Large variability
		I06 / Oe		Large variability
		I10 / Oe		Large variability
	FD	I01 / C	10412–37,28	high routine value
		I46 / BC	10108–16,20	high routine value
		S14 / Bs	10108–2,6	high FD value
		I06 / Oe	10301–24,29	high value
	PD	S09 / BC	10412–21,6	high PD value
	AS	A	19207–8,11	low audit value
		Bs	10202–2,37	high audit value
		Oa	10404–23,37	large variability
SP_SUR	S/H	I02 / Bw		large variability
	FD	I11 / Bw	19213–15,31	high FD value
	PD	I37 / Bg	10202–12,18	low routine value
		S09 / Cr	19415–9,42	large variability
		S10 / Bs	10205–8,13	large variability
	AS	A	19204–8,11	high audit value
SAND	S/H	I38 / Bw		large variability
	PD	I05 / Bw	10302–21,22	high FD value
		S02 / Bw	10406–8,17	large variability
	AS	Bw	10210–2,15	large variability
VCOS	S/H	S10 / Bw		large variability
		S10 / C		large variability
	FD	I29 / Bw	10501–15,24	high FD value
		S10 / Bw	10106–12,7	large variability
	PD	S02 / C	10110–38,36	high value
		S02 / C	10409–23,35	large variability
COS	FD	H03 / C	19208–27,24	high FD value
		I29 / Bw	10501–15,24	high FD value
		S02 / BC	10409–32,7	high routine value
	PD	E03 / Bhs	19207–2,23	large variability
		I05 / Bw	10302–21,22	large variability
		I37 / Bg	10202–18,12	large variability
MS	FD	S02 / Bc	10409–32,7	large variability
	PD	I05 / Bw	10302–21,22	high PD value
		I33 / Bx	10502–25,19	large variability
FS	S/H	I38 / Bw		large variability
		S01 / Bc		large variability
	FD	E02 / C	10403–36,2	large variability
		I21 / Cr	10301–2,6	high FD value
		I29 / Bw	10501–15,24	low FD value
	PD	I05 / Bw	10302–21,22	high PD value
		S02 / Bw	10406–17,8	large variability
	AS	Bs	10409–10,28	low audit value
		Bw	10210–2,15	high audit value
VFS	S/H	I40 / A		large variability
		S16 / C		large variability
	PD	I05 / Bw	10302–21,22	large variability
		I33 / Bx	10502–25,19	low routine value
	AS	C	10201–20,37	high audit value
SILT	S/H	I38 / Bw		large variability
		S10 / Bw		large variability

(continued)

Appendix D. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
	PD	I05 / Bw	10302-21,22	low PD value
		S02 / Bw	10406-17,8	low PD value
	AS	Bw	10210-2,15	high audit value
COSI	S/H	S10 / Bw		large variability
	FD	I29 / Bw	10501-15,24	low FD value
	PD	I05 / Bw	10302-21,22	low PD value
		S02 / Bw	10406-17,8	low PD value
FSI	S/H	I38 / A		large variability
		I38 / Bw		large variability
	FD	I01 / A	10405-31,33	high FD value
		I42 / Bw	10106-19,6	large variability
	PD	I05 / Bw	10302-21,22	low PD value
	AS	A	19207-9,40	large variability
CLAY	FD	I46 / Bw	10104-10,22	high routine value
	AS	Bs	10102-5,18	low audit value
		Bw	10210-2,15	low audit value
PH_H20	S/H	I25 / Oa		large variability
	FD	I06 / A	10211-9,16	large variability
		I38 / Bg	10202-30,29	large variability
		S17 / BL	10104-33,27	large variability
	PD	I11 / C	10211-8,21	high FD value
		I25 / Bx	10501-7,25	large variability
		IA6 / Cr	10105-31,7	large variability
	AS	Bs	10109-35,5	low audit value
		C	10211-10,18	low audit value
		Oa	10104-30,15	low audit value
PH_002M	S/H	I25 / Oa		large variability
	FD	I01 / Cg	10404-4,19	high routine value
		I02 / Bg	10102-40,30	high FD value
		I38 / Bg	10202-30,29	large variability
	PD	I42 / C	10107-18,11	large variability
	AS	Bw	10210-2,15	high audit value
		C	10305-4,12	large variability
PH_01M	S/H	I25 / Oa		large variability
	FD	I02 / C	12407-13,26	low routine value
	PD	I46 / Cr	10105-31,7	large variability
		S10 / Bs	10205-8,13	large variability
	AS	Bw	10403-17,5	low audit value
		Bw	10110-26,18	high audit value
		C	10211-10,11	large variability
		C	10305-4,12	large variability
CA_CL	FD	I33 / Bw	10502-34,7	high routine value
		I38 / Bg	10202-30,29	high FD value
		S13 / Bh	10211-22,12	high value
		H02 / Oa	10414-31,6	large variability
	PD	I25 / Bx	10504-33,16	large variability
	AS	A	19408-10,34	high audit value
		Bs	10302-35,37	low audit value
MG_CL	S/H	H02 / Oa		large variability
		I38 / Cg		large variability
	FD	I01 / C	10404-24,15	high FD value
		I38 / Bg	10202-30,29	large variability
		H03 / Oe	10411-19,4	large variability
		S18 / Oa	10109-8,2	low FD value

(continued)

Appendix D. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
	PD	I02 / C	10407–20,33	high value
		I25 / Bx	10501–7,25	large variability
		I25 / Bx	10504–33,16	large variability
		I42 / C	10107–18,11	large variability
		I46 / Cr	10105–31,7	large variability
	AS	A	19408–10,34	low audit value
		Bw	10503–21,37	low audit value
		Bs	10302–35,37	low audit value
		Oa	10114–21,29	low audit value
K_CL	S/H	I05 / A		large variability
	FD	I33 / Bw	10502–34,7	high routine value
		H03 / Oe	10411–19,4	high FD value
	PD	I02 / Bg	10113–29,19	large variability
		S15 / Cr	10108–14,5	large variability
	AS	C	10105–9,19	high audit value
		Oa	10114–21,29	low audit value
NA_CL	S/H	E06 / C		large variability
		I33 / Bx		large variability
		I37 / Oa		large variability
		I37 / Oe		large variability
	FD	I38 / Oa	10109–19,21	high routine value
	PD	I09 / Cr	10414–14,23	high routine value
		S02 / C	10103–5,12	high PD value
		S09 / Bc	10412–21,6	high routine value
	AS	Bw	10503–21,37	high audit value
		C	10501–14,39	low audit value
CA_OAC	S/H	H03 / Oa		large variability
		I02 / A		large variability
		I46 / A		large variability
		I46 / Oa		large variability
	FD	I46 / A	10108–37,34	high routine value
		I46 / Bw	10105–30,33	large variability
		I38 / Oa	10109–19,21	large variability
	PD	I33 / Bx	10502–25,19	large variability
	AS	Oa	10404–23,37	large variability
		Oa	10504–2,36	low audit value
MG_OAC	S/H	H02 / Oa		large variability
		I46 / A		large variability
	FD	I46 / A	10108–37,34	high routine value
		I46 / Bw	10105–30,33	low routine value
		H02 / Oa	10414–31,6	large variability
	PD	I46 / Cr	10105–31,7	large variability
		I42 / C	10107–18,11	high value
	AS	A	19208–9,40	high audit value
		Bw	10103–11,22	low audit value
		Oa	10404–23,27	large variability
		Oa	10504–2,36	large variability
K_OAC	S/H	E05 / Oe		large variability
		I05 / A		large variability
		S01 / Oa		large variability
		S09 / Oa		large variability
		S11 / A		large variability
		S18 / Oa		large variability
	FD	E05 / Bhs	40103–37,34	large variability
		H03 / Oe	10411–19,4	high FD value
	PD	I25 / Bx	10504–33,16	large variability
		I46 / Cr	10105–31,7	large variability

(continued)

Appendix D. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
	AS	A	19415–13,31	low audit value
		Bw	10103–11,22	high audit value
		Oa	10504–2,36	low audit value
NA_OAC	S/H	E06 / C		large variability
		I37 / Oa		large variability
		I37 / Oe		large variability
	FD	E06 / C	10214–34,24	large variability
	AS	Bs	10109–5,35	low audit value
		Bs	10502-15,33	high audit value
		Bw	10103–11,22	high audit value
		Bw	10417–15,28	high audit value
CEC_CL	S/H	I37 / Oa		large variability
		I46 / A		large variability
		S14 / Bhs		large variability
	FD	E05 / Bhs	10103–37,34	large variability
		E05 / Oa	10412–18,4	large variability
		H03 / Oe	10406–37,12	low FD value
		S18 / Oa	10109–8,2	low FD value
	PD	I46 / Cr	10105–31,7	large variability
	AS	Oa	10104–15,30	low audit value
CEC_OAC	FD	I40 / C	10211–7,35	high routine value
		H01 / Oa	10411–8,29	low routine value
		H02 / Oa	10414–31,6	low FD value
		S01 / Oa	10111–12,9	large variability
	PD	I06 / A	10215–19,2	large variability
		S02 / C	10110–38,36	high routine value
	AS	Bs	10202–2,37	large variability
		Bw	10107–8,15	large variability
		Bw	10403–5,17	large variability
		Oa	10114–21,29	low audit value
AC_KCL	S/H	S09 / Oe		large variability
	FD	E05 / A	10410–21,12	large variability
		I29 / Bw	10504–32,24	high FD value
		I38 / Oa	10109–23,27	high FD value
	PD	S02 / Bc	10417–22,7	high PD value
AC_BACL	S/H	S12 / Bhs		large variability
		H01 / Oi		large variability
	FD	E06 / C	10413–20,26	high FD value
		S10 / BC	10103–23,29	low FD value
		I38 / Oa	19204–42,23	low routine value
	PD	I01 / C	19204–3,41	high routine value
		S02 / BC	10417–22,7	large variability
		S14 / Cr	10203–10,16	high routine value
	AS	Bs	10411–6,33	large variability
		Oa	10114–21,29	large variability
AL_KCL	S/H	E05 / A		large variability
	FD	I38 / Oa	10109–23,27	high FD value
	PD	I06 / A	10215–19,2	high PD value
		I25 / Bx	10504–33,16	large variability
		S05 / Bhs	10413–14,36	large variability
	AS	Bs	10302–35,37	low audit value
		Oa	10214–4,27	high audit value
CA_CL2	S/H	H01 / Oe		large variability
		H01 / Oi		large variability
		S09 / E		large variability

(continued)

Appendix D. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
	FD	I33 / Bw	19505–12,29	large variability
		H03 / Oe	10402–10,23	large variability
		H03 / Oe	10406–37,12	low routine value
		I06 / Oe	10301–24,29	low routine value
	PD	I11 / C	10211–8,21	large variability
	AS	C	10401–4,21	large variability
		Oa	10104–15,30	low audit value
		Oa	10114–21,29	low audit value
MG_CL2	S/H	H02 / Oa		large variability
		S01 / Oe		large variability
		S02 / Oe		large variability
	FD	I11 / Bw	10211–31,6	high routine value
		H02 / Oa	10503–31,25	low FD value
		H03 / Oe	10406–37,12	low routine value
	PD	E02 / Cg	10102–14,27	low PD value
	AS	A	19505–13,36	low audit value
		C	10205–2,19	high audit value
K_CL2	FD	I11 / Bw	10211–31,6	high routine value
		H01 / Oe	10413–33,2	low FD value
		H02 / Oa	10503–31,25	low FD value
		H03 / Oe	10411–19,4	high FD value
		S01 / Oa	10111–12,9	large variability
	PD	I46 / BC	10104–23,18	high routine value
	AS	Bw	10107–8,15	low audit value
NA_CL2	S/H	E06 / C		large variability
		H03 / Oa		large variability
		I37 / Oa		large variability
		I37 / Oe		large variability
	FD	H02 / A	10411–2,23	large variability
		I38 / Oa	10109–19,21	high routine value
	PD	I02 / Cr	10101–8,1	high routine value
		I42 / C	10107–18,11	large variability
	AS	Oa	10504–2,36	large variability
FE_CL2	AS	A	19415–13,31	large variability
		C	10108–26,31	large variability
AL_CL2	S/H	S01 / Bh		large variability
	FD	S12 / Bhs	10417–10,18	high routine value
		I38 / Oa	10109–23,27	large variability
		I38 / Oa	10109–19,21	low value
	AS	Bs	10209–7,8	large variability
		C	10105–9,19	high audit value
FE_PYP	S/H	S05 / Bhs		large variability
		S12 / Bh		large variability
	FD	I46 / A	10108–37,34	large variability
		S05 / Bg	10403–16,38	large variability
	PD	S05 / Bg	10403–16,33	large variability
	AS	Bs	10416–8,25	large variability
		Bw	10503–21,37	large variability
		Oa	10404–23,37	high audit value
AL_PYP	S/H	S01 / Bhs		large variability
	FD	I11 / Bw	10303–17,7	high FD value
		S09 / Bs	10401–16,24	large variability
		S12 / Bs	10404–25,16	large variability
		I38 / Oa	10109–23,27	low routine value

(continued)

Appendix D. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
	AS	A	19208-2,33	high audit value
		Bs	10416-8,25	low audit value
		Oa	10404-23,37	high audit value
FE_OA	S/H	S05 / Bhs		large variability
		S05 / Oa		large variability
	FD	S09 / Bs	10406-15,23	high FD value
	AS	Bs	10202-2,37	low audit value
		C	10205-2,19	high audit value
AL_AO	S/H	S05 / Oe		large variability
		S14 / Bhs		large variability
	FD	S05 / Bg	10413-41,35	large variability
		S13 / Bs	10102-15,12	high F.D value
FE_CD	S/H	S05 / Bhs		large variability
	PD	I05 / Bw	10302-21,22	large variability
		S05 / Bhs	10413-14,36	large variability
		S10 / Bs	10205-8,13	large variability
	AS	A	19505-13,36	high audit value
		C	10413-8,18	high audit value
AL_CD	S/H	S13 / Bhs		large variability
		S14 / Bhs		large variability
		S05 / Oa		large variability
	FD	S14 / Bs	10404-5,12	large variability
	PD	S02 / BC	10417-22,7	large variability
		S10 / Bs	10205-8,13	large variability
	AS	Bs	10202-2,37	large variability
		Bw	10113-11,33	low audit value
SO4_H2O	S/H	H02 / Oa		large variability
		H02 / Oe		large variability
		I40 / C		large variability
	FD	I40 / Ap	10211-33,15	high routine value
		S14 / Bs	10410-3,37	high FD value
		H03 / Oe	10402-10,23	high FD value
	PD	I33 / Bx	19505-40,22	high PD value
		S02 / C	10103-5,12	high PD value
	AS	A	19207-9,40	large variability
		A	19505-13,36	large variability
		Oa	10114-21,29	large variability
SO4_PO4	S/H	H02 / Oa		large variability
		I06 / Bw		large variability
		S09 / Bw		large variability
		S10 / BC		large variability
	FD	H03 / Oe	10402-10,23	high FD value
	PD	I05 / Bw	10302-21,22	low PD value
	AS	A	19213-20,34	high audit value
SO4_0	S/H	H02 / Oa		large variability
		H02 / Oe		large variability
		H03 / Oa		large variability
		H03 / Oe		large variability
	FD	H03 / Oe	10402-10,23	high FD value
	PD	I01 / C	19204-3,41	high routine value
		I05 / Bw	10302-21,22	low PD value
	AS	A	19415-13,31	high audit value
		Oa	10214-4,27	large variability
SO4_2	S/H	H02 / Oa		large variability
	FD	H03 / Oe	10402-10,23	high FD value

(continued)

Appendix D. Continued

Parameter	Data set^a	Sampling class/horizon	Batch/sample	Reason
	PD	I46 / Cr	10105–31,7	low routine value
	AS	A	19204–6,11	low audit value
		Bw	10407–14,27	low audit value
SO4_4	S/H	H02 / Oa		large variability
		H02 / Oe		large variability
		H03 / Oa		large variability
	FD	S17 / Bh	10104–33,27	high FD value
		H03 / Oe	10402–10,23	high FD value
		I38 / Oa	19204–42,23	high value
	PD	I42 / C	10107–18,11	low PD value
	AS	A	19207–9,40	high audit value
		Bs	10102–5,18	large variability
		Bw	10107–8,15	low audit value
SO4_8	S/H	H02 / Oa		large variability
		H02 / Oe		large variability
		H03 / Oa		large variability
	FD	H03 / Oe	10402–10,23	high FD value
	PD	E03 / Bhs	19207–2,23	high PD value
		I09 / C	10201–23,21	large variability
		I25 / Bx	10504–33,16	large variability
		S10 / Bs	10205–8,13	large variability
	AS	C	10201–20,37	large variability
SO4_16	S/H	H02 / Oa		large variability
		H02 / Oe		large variability
		H03 / Oe		large variability
	FD	H03 / Oe	10402–10,23	high FD value
	AS	Bw	10107–8,15	large variability
		C	10201–20,37	high audit value
SO4_32	S/H	H02 / Oa		large variability
		H02 / Oe		large variability
		H03 / Oe		large variability
		S15 / E		large variability
	FD	H03 / Oe	10402–10,23	high FD value
	PD	I06 / Bhs	10304–4,33	large variability
	AS	C	10201–20,37	large variability
		Oa	10104–15,30	high audit value
C_TOT	S/H	S05 / Bg		large variability
	FD	S05 / Bg	10413–41,35	large variability
		H01 / Oa	10409–4,25	large variability
		S02 / Oa	10417–26,16	high FD value
	PD	S02 / BC	10417–22,7	high PD value
		S10 / Bs	10205–8,13	large variability
N_TOT	S/H	S11 / A		large variability
	FD	I25 / Bw	10413–11,22	high FD value
		H01 / Oa	10403–27,19	low FD value
		S02 / Oa	10417–26,16	high FD value
	PD	S02 / Bhs	10405–19,37	high PD value
	AS	A	19408–10,34	low audit value
		A	19505–13,36	high audit value
S_TOT	S/H	H02 / Oa		large variability
		H02 / Oe		large variability
		H03 / Oe		large variability
		I37 / Oe		large variability
		S14 / Bhs		large variability
	FD	I30 / Bw	10501–36,28	high FD value
		H01 / Oe	10413–33,2	large variability

(continued)

Appendix D. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
	PD	I02 / C	10407–20,33	large variability
		S09 / Cr	10416–1,18	large variability
	AS	Bw	10103–11,22	low audit value
		Bw	10412–7,31	large variability
		Oa	10504–2,36	large variability

[a] AS = audit sample; PD = preparation duplicate; FD = field duplicate; S/H = sampling class/horizon groups of routine samples.

NOTE: Sampling class codes are as follows: FR = frigid, OTC = calcareous, SKV = skeletal concave, SKX = skeletal convex, FL = flooded, SHL = low organic shallow, ACH = high organic acid crystalline, MSH = high organic metasedimentary, ACC = low organic clayey acid crystalline, ACL = other low organic crystalline, MSL = low organic metasedimentary, OTL = other organic soils.

Appendix E

Precision Plots for Moisture, Specific Surface, and Particle Size Fractions

Following are precision plots for the routine and QA data sets from the MOIST, SP_SUR, VCOS, COS, MS, FS, VFS, COSI, and FSI parameters. Since these parameters did not have specifically established DQOs, it was decided to place the routine data plots in the appendix and separate from the audit sample/routine sample paired plots found Section 3 in the Results and Discussion of the report. Supplemental information relating to these plots can be found in Section 3 under the parameter group heading and in Appendices C and D.

MOIST

Moisture

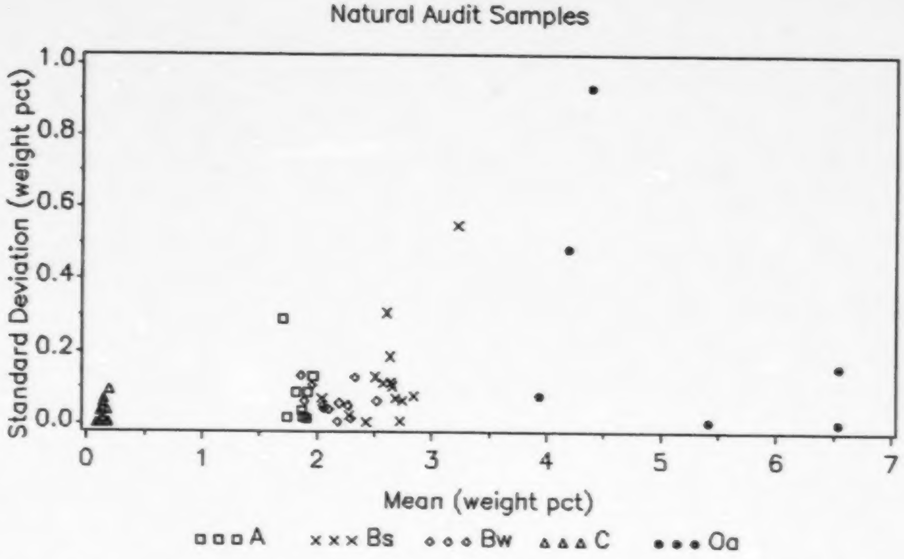
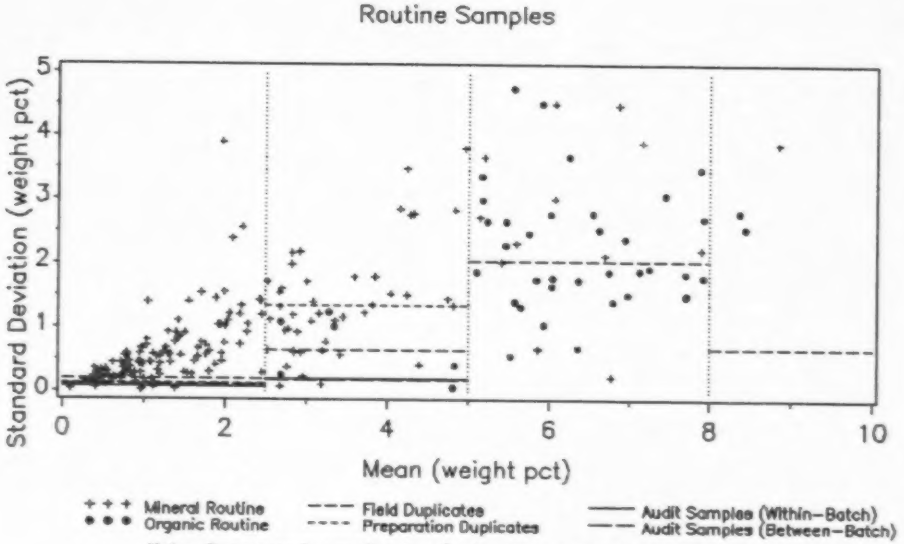


Figure E-1. Range and frequency distribution of the natural audit samples for MOIST.



Note: Seven organic sampling class/horizon groups exceed plot boundaries.

Figure E-2. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for MOIST.

SP_SUR

Specific Surface

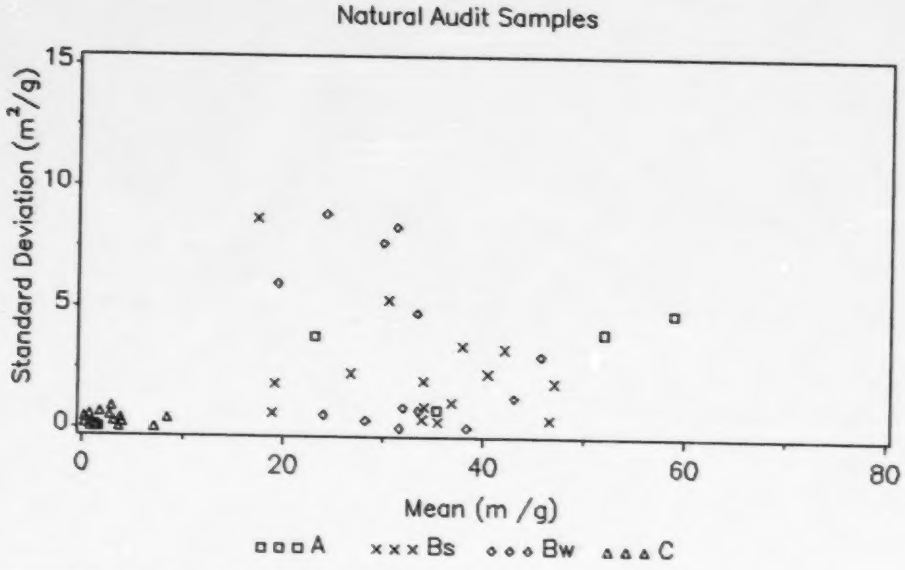
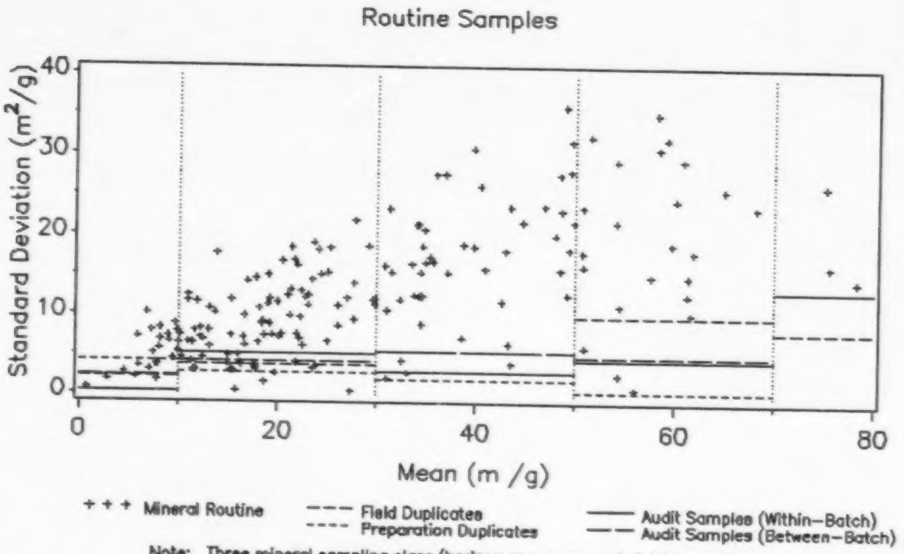


Figure E-3. Range and frequency distribution of the natural audit samples for SP_SUR.



Note: Three mineral sampling class/horizon groups exceed plot boundaries.

Figure E-4. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for SP_SUR.

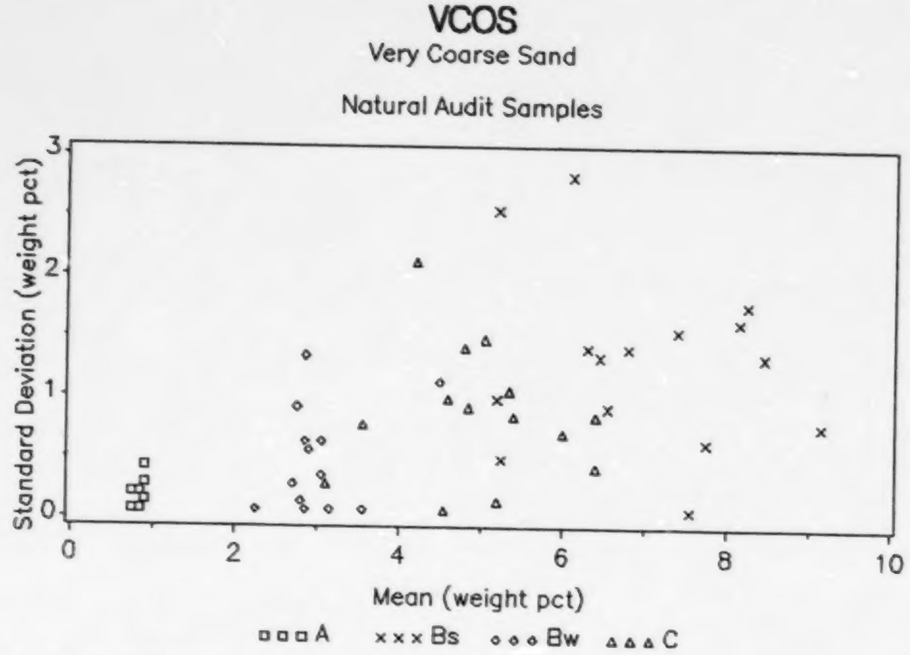
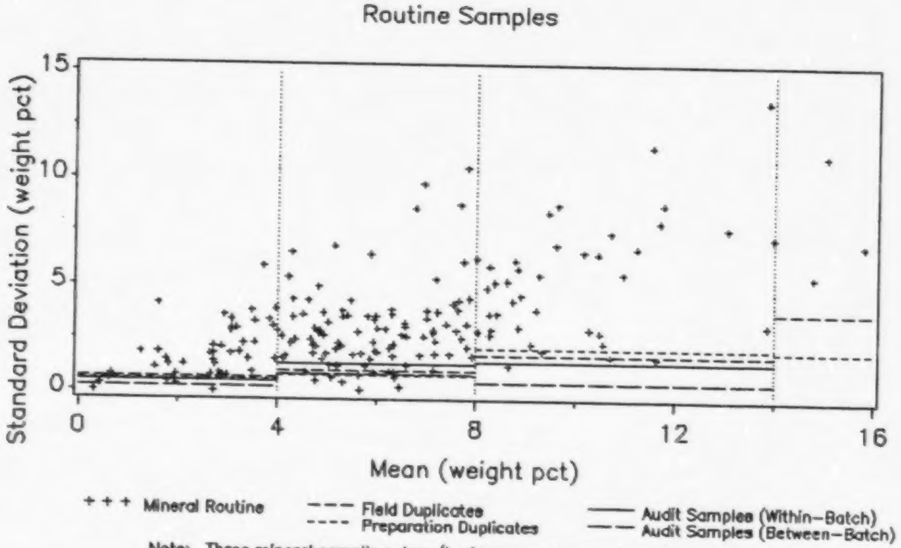


Figure E-5. Range and frequency distribution of the natural audit samples for VCOS.



Note: Three mineral sampling class/horizon groups exceed plot boundaries.

Figure E-6. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for VCOS.

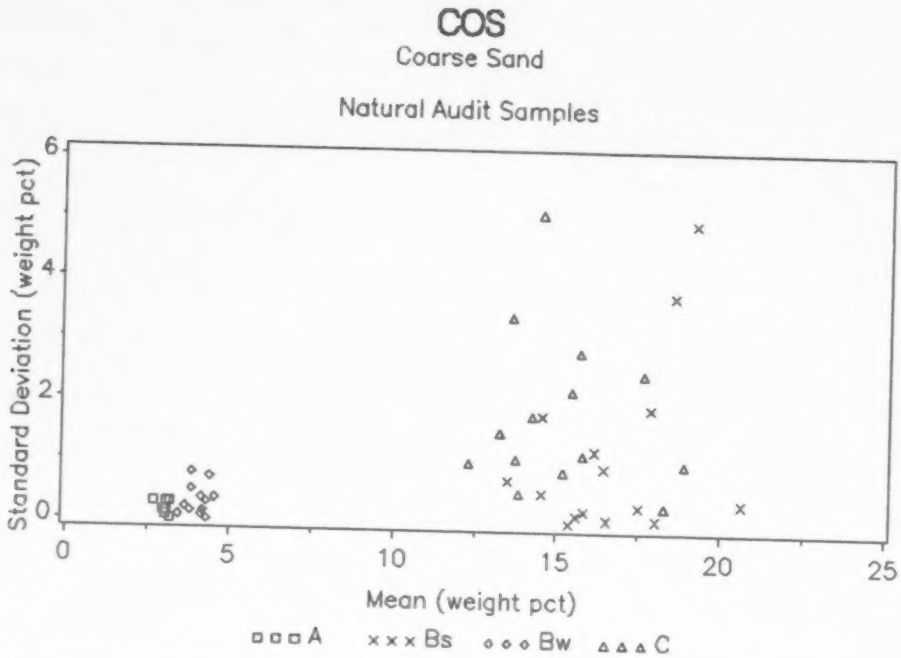
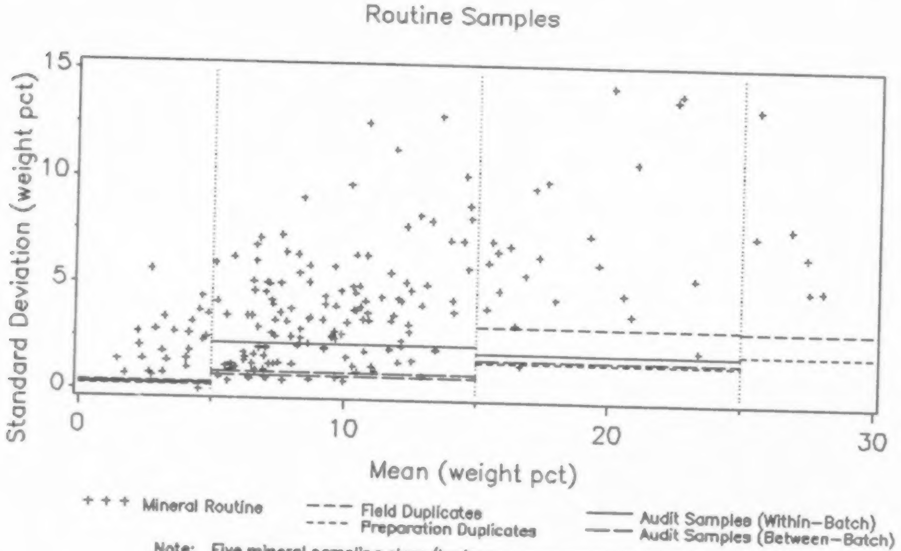


Figure E-7. Range and frequency distribution of the natural audit samples for COS.



Note: Five mineral sampling class/horizon groups exceed plot boundaries.

Figure E-8. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for COS.

MS

Medium Sand

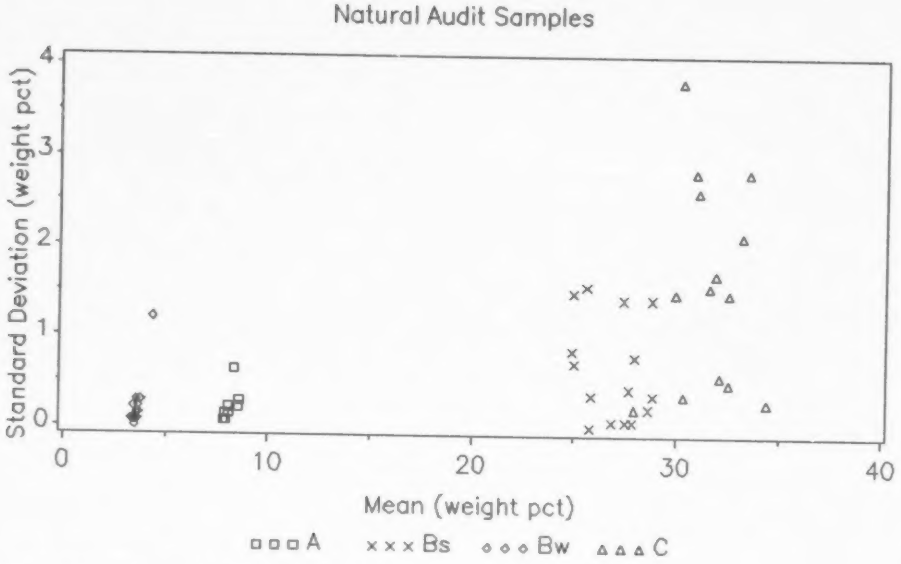
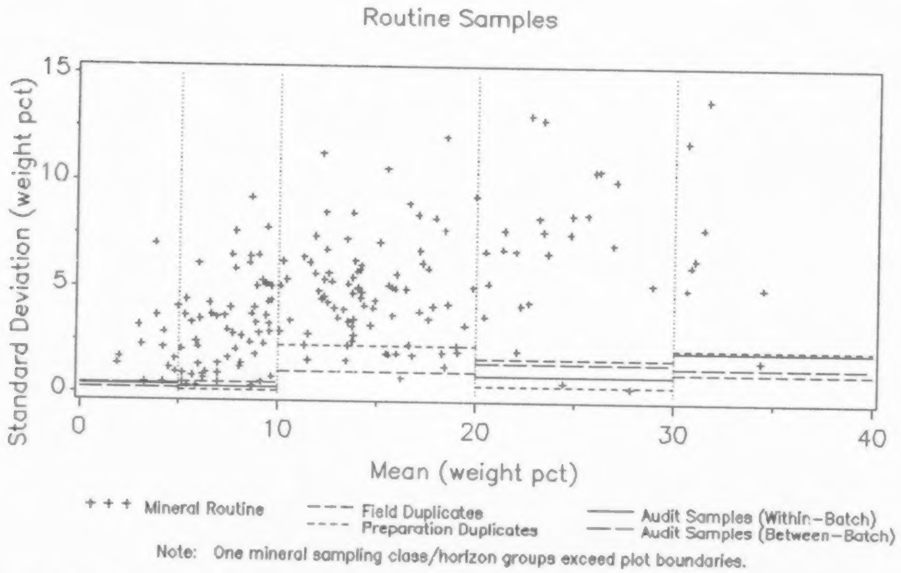


Figure E-9. Range and frequency distribution of the natural audit samples for MS.



Note: One mineral sampling class/horizon groups exceed plot boundaries.

Figure E-10. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for MS.

FS

Fine Sand

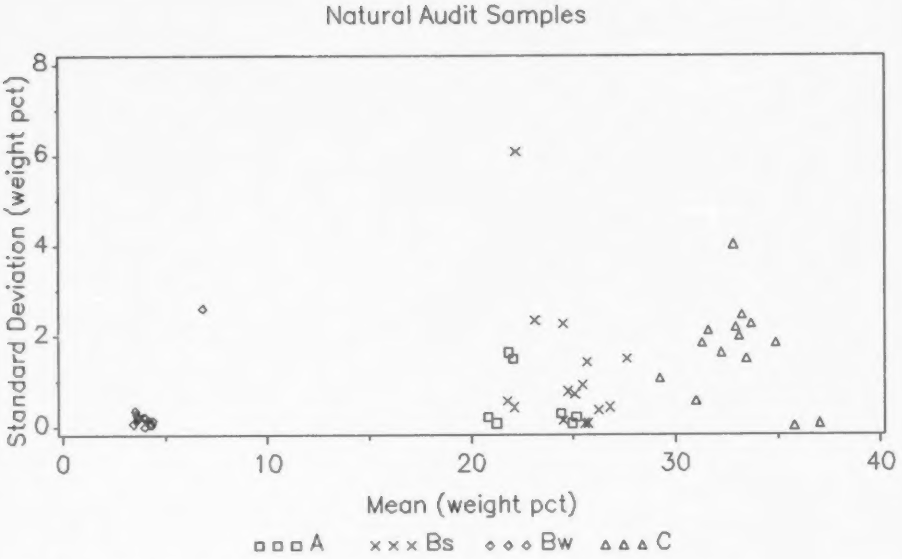
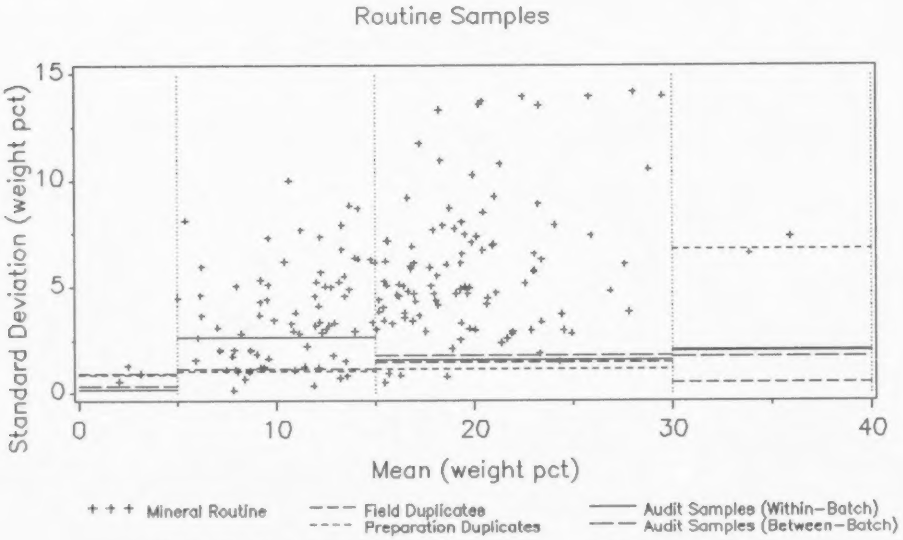


Figure E-11. Range and frequency distribution of the natural audit samples for FS.



Note: Five mineral sampling class/horizon groups exceed plot boundaries.

Figure E-12. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for FS.

VFS

Very Fine Sand

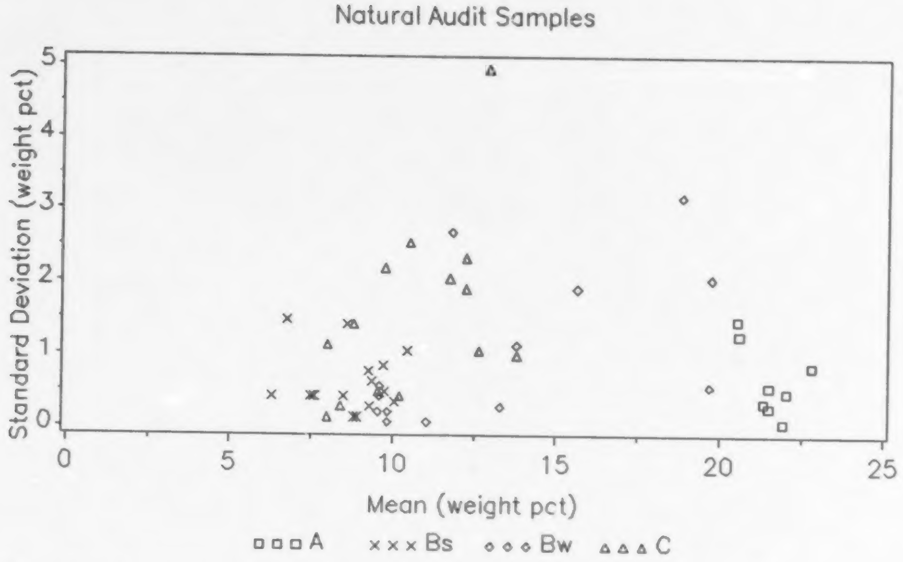
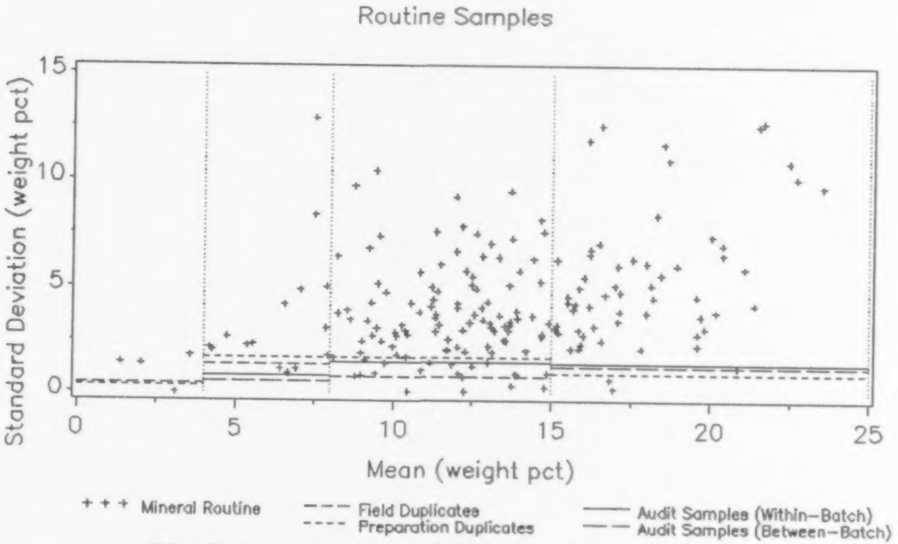


Figure E-13. Range and frequency distribution of the natural audit samples for VFS.



Note: Four mineral sampling class/horizon groups exceed plot boundaries.

Figure E-14. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for VFS.

COSI

Coarse Silt

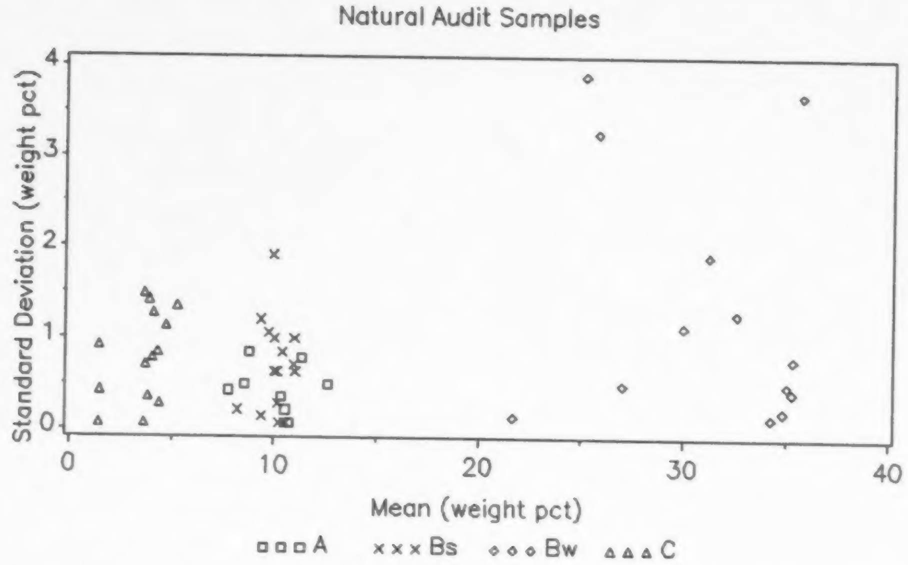
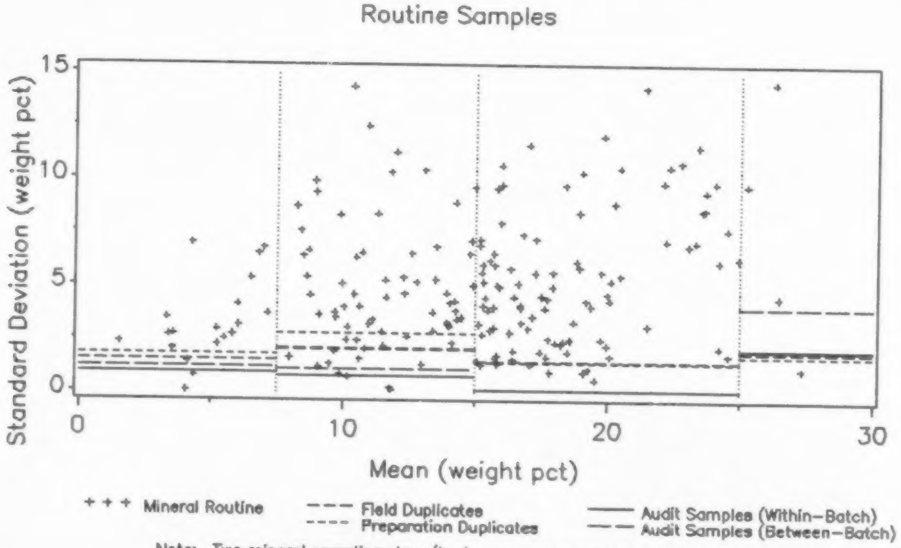


Figure E-15. Range and frequency distribution of the natural audit samples for COSI.



Note: Two mineral sampling class/horizon groups exceed plot boundaries.

Figure E-16. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for COSI.

FSI

Fine Silt

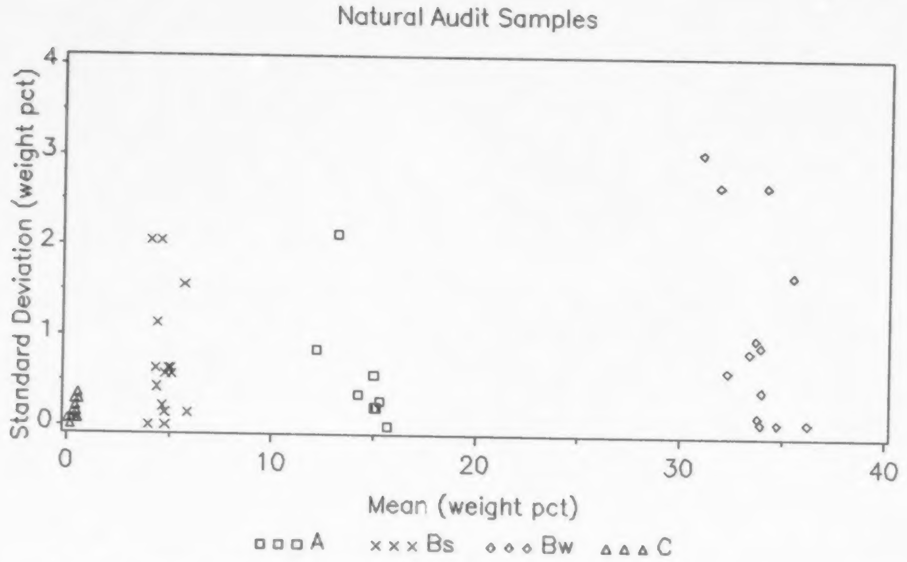
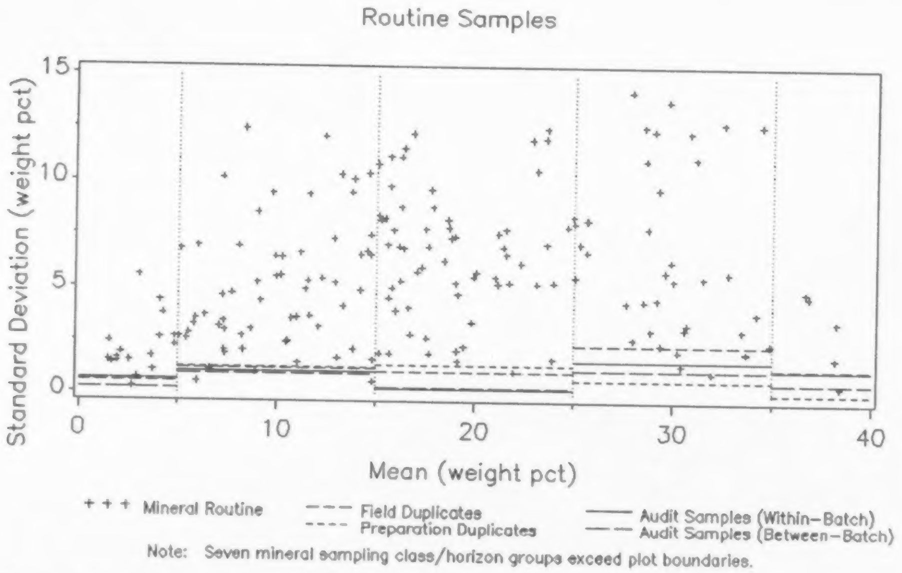


Figure E-17. Range and frequency distribution of the natural audit samples for FSI.



Note: Seven mineral sampling class/horizon groups exceed plot boundaries.

Figure E-18. Range and frequency distribution of sampling class/horizon routine data partitioned into windows and their relation to pooled precision estimates for FSI.

Appendix F

General Statistics for the 51 Analytical Parameters

Appendix F is a summary table of the soil chemistry and physical data for the Northeastern Soil Survey. Included are data sorted by laboratory and by audit sample type for mean concentration, standard deviation, and laboratory difference from the interlaboratory mean. Supplemental information relating to this table can be found in the discussion and figures under "Precision", and "Interlaboratory Differences" in Section 2 and 3 of the report. Data are presented for each of the 51 analytical parameters in the order described in Table 1-1 of Section 1 of the report.

Appendix F. Table of General Statistics for the Analytical Parameters

Lab	Audit Sample[a]														
	Oa			A			Bs			Bw			C		
	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d
Moisture % dry wt															
1	6.54	0.09	1.37	1.89	0.08	0.04	2.61	0.10	0.00	1.94	0.10	0.19*[b]	0.13	0.04	0.02
2	4.29	0.62	0.88	1.81	0.15	0.04	2.63	0.15	0.01	2.28	0.18	0.16*	0.16	0.03	0.02
3	–[c]	–	–	–	–	–	2.25	0.18	0.37*	2.05	0.05	0.07	–	–	–
4	4.67	0.86	0.49	–	–	–	2.83	0.29	0.21*	2.25	0.06	0.13*	0.15	0.04	0.01
ALL	5.17	1.17		1.85	0.13		2.62	0.29		2.12	0.20		0.14	0.04	
Specific Surface m^2/g															
1	–	–	–	84.6	154.	21.0*	19.0	1.13	14.4*	30.5	8.67	1.40	1.43	1.43	1.50*
2	–	–	–	42.3	15.2	21.1*	35.0	5.43	1.60	36.7	7.15	4.90*	2.04	0.66	0.89*
3	–	–	–	–	–	–	42.6	6.74	9.20*	33.5	0.75	1.60	–	–	–
4	–	–	–	–	–	–	32.0	9.30	1.40	27.2	6.57	4.70*	5.28	2.21	2.30*
ALL	–	–		63.4	108.		33.4	9.56		31.9	7.99		2.94	2.40	
Total Sand (2.0 - 0.5 mm) % dry wt															
1	–	–	–	54.4	0.37	2.40	83.4	0.80	0.63	24.0	0.51	4.10*	95.1	1.11	0.37
2	–	–	–	59.2	0.59	2.40	83.4	0.93	0.60	33.3	2.32	5.20*	95.9	1.64	0.47
3	–	–	–	–	–	–	84.7	1.13	0.68	26.2	0.28	1.90*	–	–	–
4	–	–	–	–	–	–	84.5	0.97	0.45	28.7	3.84	0.60	95.6	0.82	0.16
ALL	–	–		56.8	2.52		84.1	1.09		28.1	4.52		95.5	1.16	
Very Coarse Sand (2.0 - 1.0 mm) % dry wt															
1	–	–	–	0.84	0.19	0.01	7.17	0.93	0.21	2.95	0.40	0.07	4.96	1.04	0.00
2	–	–	–	0.85	0.16	0.01	7.28	1.22	0.31	3.17	1.01	0.16	4.57	1.82	0.39*
3	–	–	–	–	–	–	7.18	2.11	0.21	3.15	0.07	0.13	–	–	–
4	–	–	–	–	–	–	6.45	1.97	0.52*	2.88	0.79	0.14	5.20	0.97	0.24
ALL	–	–		0.84	0.17		6.97	1.63		3.02	0.70		4.96	1.19	
Coarse Sand (1.0 - 0.5 mm) % dry wt															
1	–	–	–	3.10	0.15	0.03	15.2	1.27	1.50*	4.30	0.24	0.23*	15.5	2.10	0.28
2	–	–	–	3.04	0.27	0.03	15.9	0.94	0.80*	3.82	0.47	0.25*	14.6	2.74	0.58
3	–	–	–	–	–	–	18.4	3.29	1.70*	4.30	0.00	0.23*	–	–	–
4	–	–	–	–	–	–	17.1	2.40	0.40	3.95	0.47	0.12	15.2	2.94	0.01
ALL	–	–		3.07	0.21		16.7	2.30		4.07	0.42		15.2	2.49	
Medium Sand (0.5 - 0.25 mm) % dry wt															
1	–	–	–	7.95	0.13	0.22	26.3	0.61	0.60	3.46	0.08	0.16	31.7	1.56	0.10
2	–	–	–	8.39	0.37	0.22	25.3	0.90	1.60*	3.60	0.15	0.02	29.4	1.34	2.20*
3	–	–	–	–	–	–	28.0	0.85	1.10	3.65	0.21	0.03	–	–	–
4	–	–	–	–	–	–	28.2	0.81	1.30	3.92	0.66	0.29*	32.8	2.30	1.20
ALL	–	–		8.17	0.35		26.9	1.55		3.62	0.36		31.6	2.16	
Fine Sand (0.25 - 0.1 mm) % dry wt															
1	–	–	–	21.5	0.98	1.70*	25.2	1.08	0.48	3.57	0.19	0.56*	32.2	1.68	0.80
2	–	–	–	24.9	0.33	1.70*	25.6	0.57	0.87	4.20	0.21	0.07	35.4	2.06	2.30*
3	–	–	–	–	–	–	23.7	3.64	1.05	4.00	0.00	0.13	–	–	–
4	–	–	–	–	–	–	24.3	2.38	0.43	5.02	1.85	0.89*	32.7	2.64	0.30
ALL	–	–		23.2	1.87		24.7	2.20		4.13	1.01		33.0	2.42	
Very Fine Sand (0.1 - 0.05 mm) % dry wt															
1	–	–	–	21.0	0.89	0.54*	9.47	0.71	0.76*	9.69	0.29	3.57*	10.8	1.98	0.20
2	–	–	–	22.1	0.66	0.54*	9.45	0.54	0.73*	18.5	2.41	5.20*	11.6	2.56	0.99*
3	–	–	–	–	–	–	7.47	1.04	1.25*	11.0	0.07	2.21*	–	–	–
4	–	–	–	–	–	–	8.44	1.55	0.28*	13.0	1.61	0.29	9.79	2.70	0.84*
ALL	–	–		21.5	0.94		8.72	1.30		13.3	4.05		10.6	2.40	

(continued)

Appendix F. Continued

Lab	Audit Sample[a]														
	Oa			A			Bs			Bw			C		
	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d
							Total Silt (0.05 - 0.002 mm) % dry wt								
1	–	–	–	26.6	1.04	2.00*	15.9	1.09	1.00	68.8	0.42	3.90*	4.71	1.11	0.73*
2	–	–	–	22.6	0.82	2.00*	14.8	1.23	0.01	59.0	1.94	5.90*	2.82	1.74	1.16*
3	–	–	–	–	–	–	14.3	1.43	0.52	65.0	0.57	0.10	–	–	–
4	–	–	–	–	–	–	14.8	1.00	0.09	66.1	3.15	1.20	3.80	1.22	0.18
ALL	–	–		24.6	2.30	2.00	14.9	1.21	0.27	64.9	4.52		3.98	1.45	
							Coarse Silt (0.05 - 0.02 mm) % dry wt								
1	–	–	–	11.3	0.95	1.20*	11.0	0.70	0.91	35.0	0.53	3.90*	4.31	0.95	0.74*
2	–	–	–	8.90	1.08	1.20*	9.79	0.90	0.30	24.9	2.86	6.20*	2.43	1.58	1.13*
3	–	–	–	–	–	–	9.73	1.22	0.36	32.6	1.27	1.50	–	–	–
4	–	–	–	–	–	–	10.2	0.69	0.15	32.3	3.30	1.20	3.36	1.23	0.21*
ALL	–	–		10.1	1.60	1.20	10.1	0.94	0.34	31.1	4.83	3.80	3.57	1.37	0.63
							Fine Silt (0.02 - 0.005 mm) % dry wt								
1	–	–	–	15.3	0.31	0.82*	4.85	0.45	0.08	33.8	0.60	0.02	0.41	0.19	0.00
2	–	–	–	13.7	1.45	0.82*	5.07	1.15	0.30	34.1	2.19	0.32	0.33	0.31	0.07
3	–	–	–	–	–	–	4.62	0.57	0.15	32.3	0.64	1.40	–	–	–
4	–	–	–	–	–	–	4.52	0.84	0.25	33.8	2.64	0.01	0.44	0.14	0.04
ALL	–	–		14.5	1.32	0.82	4.77	0.88	0.22	33.8	1.75	0.22	0.40	0.20	0.03
							Total Clay (< 0.002 mm) % dry wt								
1	–	–	–	19.0	0.80	0.36	0.70	0.36	0.38	7.27	0.36	0.22	0.17	0.13	0.40*
2	–	–	–	18.2	0.71	0.36	1.69	0.86	0.61	7.70	1.43	0.65*	1.22	0.95	0.65*
3	–	–	–	–	–	–	0.95	0.40	0.13	8.85	0.92	1.80*	–	–	–
4	–	–	–	–	–	–	0.71	0.25	0.37	5.20	1.38	1.85*	0.67	0.84	0.10*
ALL	–	–		18.6	0.82	0.36	1.08	0.70	0.40	7.05	1.51		0.57	0.76	
							pH in H_2O								
1	3.46	0.22	0.13	4.53	0.04	0.00	4.36	0.09	0.13	5.02	0.04	0.06	5.19	0.27	0.14
2	3.71	0.02	0.12	4.52	0.03	0.00	4.52	0.04	0.03	5.14	0.03	0.06	5.56	0.08	0.24
3	–	–	–	–	–	–	4.50	0.04	0.01	5.15	0.01	0.06	–	–	–
4	3.60	0.04	0.02	–	–	–	4.50	0.03	0.01	5.09	0.06	0.00	5.34	0.09	0.02
ALL	3.59	0.16	.52	0.04	–		4.49	0.07	–	5.08	0.06	–	5.32	0.24	–
							pH in 0.002M $CaCl_2$								
1	3.16	0.16	0.08	4.23	0.03	0.01	4.13	0.01	0.02	4.65	0.10	0.06	4.91	0.06	0.05
2	3.27	0.04	0.03	4.21	0.01	0.01	4.14	0.02	0.00	4.72	0.02	0.02	4.97	0.12	0.01
3	–	–	–	–	–	–	4.14	0.03	0.00	4.75	0.02	0.04	–	–	–
4	3.29	0.07	0.05	–	–	–	4.15	0.04	0.01	4.77	0.07	0.06	5.01	0.05	0.05
All	3.24	0.11		4.22	0.02		4.14	0.03		4.71	0.09		4.96	0.08	
							pH in 0.01M $CaCl_2$								
1	3.00	0.04	0.01	4.02	0.04	0.04	3.96	0.03	0.03	4.57	0.03	0.04	4.72	0.12	0.04
2	3.00	0.01	0.00	3.95	0.02	0.03	3.93	0.02	0.01	4.46	0.52	0.07	4.87	0.03	0.12
3	–	–	–	–	–	–	3.94	0.03	0.00	4.58	0.05	0.04	–	–	–
4	3.02	0.02	0.01	–	–	–	3.93	0.07	0.01	4.56	0.07	0.02	4.73	0.11	0.03
ALL	3.01	0.02		3.99	0.05		3.94	0.05		4.54	0.28		4.76	0.12	
							Ca in NH_4Cl meq/100g								
1	1.43	0.39	0.34*	0.29	0.04	0.02	0.32	0.03	0.04*	0.29	0.05	0.02	0.08	0.02	0.01
2	1.55	0.04	0.23*	0.25	0.02	0.02	0.25	0.06	0.03*	0.24	0.05	0.03*	0.08	0.03	0.02
3	–	–	–	–	–	–	0.27	0.04	0.01	0.29	0.00	0.02	–	–	–
4	2.34	0.13	0.57*	–	–	–	0.30	0.10	0.02	0.28	0.03	0.01	0.08	0.01	0.00
ALL	1.77	0.48		0.27	0.04		0.28	0.07		0.27	0.05		0.07	0.02	

(continued)

Appendix F. Continued

Lab	Audit Sample[a]														
	Oa			A			Bs			Bw			C		
	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d
Mg in NH$_4$Cl meq/100g															
1	0.27	0.03	0.11*	0.22	0.03	0.00	0.06	0.00	0.01	0.05	0.05	0.00	0.03	0.02	0.00
2	0.36	0.05	0.01	0.22	0.01	0.00	0.05	0.01	0.00	0.05	0.01	0.00	0.03	0.01	0.00
3	–	–	–	–	–	–	0.05	0.01	0.00	0.04	0.01	0.01	–	–	–
4	0.50	0.03	0.12*	–	–	–	0.06	0.01	0.01	0.06	0.01	0.01	0.03	0.00	0.00
ALL	0.38	0.10		0.22	0.02		0.05	0.01		0.05	0.03		0.03	0.01	
K in NH$_4$Cl meq/100g															
1	0.28	0.06	0.04*	0.24	0.02	0.00	0.02	0.01	0.02	0.06	0.01	0.00	0.03	0.02	0.00
2	0.31	0.06	0.01	0.24	0.02	0.00	0.04	0.02	0.01	0.06	0.01	0.00	0.03	0.01	0.00
3	–	–	–	–	–	–	0.03	0.01	0.00	0.07	0.00	0.01	–	–	–
4	0.37	0.03	0.05*	–	–	–	0.03	0.00	0.00	0.06	0.00	0.00	0.03	0.00	0.00
ALL	0.32	0.06		0.24	0.02		0.03	0.02		0.06	0.01		0.03	0.01	
Na in NH$_4$Cl meq/100g															
1	0.18	0.03	0.00	0.04	0.01	0.01	0.00	0.03	0.02	0.06	0.06	0.02	0.01	0.03	0.01
2	0.18	0.02	0.00	0.02	0.01	0.01	0.01	0.00	0.00	0.02	0.00	0.02	0.00	0.01	0.01
3	–	–	–	–	–	–	0.03	0.01	0.01	0.02	0.02	0.02	–	–	–
4	0.19	0.01	0.01	–	–	–	0.02	0.00	0.00	0.04	0.01	0.00	0.01	0.00	0.01
ALL	0.18	0.02		0.03	0.02		0.02	0.01		0.04	0.04		0.00	0.02	
Ca in NH$_4$OAC meq/100g															
1	1.17	0.30	0.03	0.27	0.03	0.01	0.24	0.04	0.03*	0.29	0.07	0.04*	0.08	0.03	0.01
2	0.94	0.28	0.21*	0.26	0.02	0.01	0.20	0.02	0.02	0.22	0.04	0.03*	0.05	0.02	0.02
3	–	–	–	–	–	–	0.23	0.05	0.02	0.26	0.02	0.01	–	–	–
4	1.33	0.12	0.18*	–	–	–	0.21	0.02	0.00	0.23	0.02	0.02	0.08	0.01	0.00
ALL	1.15	0.28		0.27	0.03		0.21	0.03		0.25	0.06		0.07	0.03	
Mg in NH$_4$OAC meq/100g															
1	0.30	0.08	0.05*	0.24	0.03	0.01	0.06	0.02	0.01	0.05	0.02	0.00	0.02	0.02	0.00
2	0.33	0.08	0.02	0.22	0.02	0.01	0.04	0.01	0.01	0.05	0.01	0.00	0.03	0.01	0.00
3	–	–	–	–	–	–	0.05	0.01	0.00	0.06	0.01	0.01	–	–	–
4	0.42	0.04	0.07*	–	–	–	0.05	0.00	0.00	0.05	0.00	0.00	0.03	0.01	0.01
ALL	0.35	0.08		0.23	0.03		0.05	0.01		0.05	0.01		0.03	0.02	
K in NH$_4$OAC meq/100g															
1	0.34	0.05	0.00	0.26	0.01	0.01	0.02	0.01	0.00	0.07	0.04	0.01	0.02	0.01	0.00
2	0.29	0.08	0.05*	0.24	0.02	0.01	0.02	0.01	0.00	0.04	0.01	0.02	0.02	0.01	0.00
3	–	–	–	–	–	–	0.04	0.01	0.01	0.07	0.00	0.01	–	–	–
4	0.39	0.01	0.05*	–	–	–	0.03	0.00	0.00	0.06	0.00	0.00	0.03	0.00	0.01
ALL	0.34	0.07		0.25	0.02		0.03	0.01		0.06	0.02		0.02	0.01	
Na in NH$_4$OAC meq/100g															
1	0.15	0.05	0.02	0.03	0.01	0.00	0.04	0.07	0.02	0.04	0.07	0.01	0.01	0.01	0.00
2	0.17	0.02	0.01	0.04	0.01	0.00	0.01	0.00	0.01	0.02	0.01	0.01	0.00	0.00	0.00
3	–	–	–	–	–	–	0.02	0.01	0.00	0.08	0.08	0.05	–	–	–
4	0.20	0.00	0.02	–	–	–	0.02	0.00	0.00	0.02	0.01	0.01	0.00	0.00	0.00
ALL	0.17	0.03		0.03	0.01		0.02	0.02		0.03	0.05		0.00	0.01	
CEC in NH$_4$Cl meq/100g															
1	17.3	3.09	3.78*	8.0	0.25	0.32	7.5	1.16	1.36*	6.0	0.67	0.81*	0.54	0.28	0.03
2	21.7	2.89	0.58	7.3	0.46	0.32	7.5	0.38	1.37*	3.7	0.12	1.44*	0.52	0.14	0.05*
3	–	–	–	–	–	–	12.9	1.40	4.00*	9.6	0.59	4.40*	–	–	–
4	24.3	0.77	3.20*	–	–	–	8.4	0.85	0.50*	4.3	0.39	0.91*	0.63	0.37	0.06*
ALL	21.1	3.76		7.7	0.49		8.9	2.25		5.2	1.71		0.57	0.29	

(continued)

Appendix F. Continued

Lab	Audit Sample[a]														
	Oa			A			Bs			Bw			C		
	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d
	CEC in NH_4OAC meq/100g														
1	82.8	11.1	1.18	18.7	0.40	1.69*	27.3	0.82	2.65*	13.9	1.18	1.35*	1.26	0.12	0.25*
2	83.9	5.97	0.16	15.4	0.74	1.62*	22.0	2.22	2.64*	10.4	1.41	2.14*	0.76	0.34	0.25*
3	–	–	–	–	–	–	26.5	2.01	1.80*	16.4	1.15	3.85*	–	–	–
4	85.4	3.47	1.40	–	–	–	25.2	2.16	0.52	11.9	0.82	0.65*	0.85	0.15	0.16*
ALL	84.0	6.92		17.0	1.77		24.7	2.80	1.46	12.5	2.17		1.00	0.29	
	KCL Acidity meq/100g														
1	3.5	1.03	6.24*	3.01	0.11	0.32*	4.24	0.27	0.43*	1.59	0.14	0.03	0.14	0.07	0.03
2	10.5	4.51	0.77*	3.64	0.19	0.32*	4.82	0.30	0.14	1.65	0.17	0.03	0.23	0.08	0.06
3	–	–	–	–	–	–	3.99	0.54	0.68*	1.67	0.07	0.05	–	–	–
4	15.2	0.95	5.50*	–	–	–	5.12	0.61	0.44*	1.62	0.21	0.00	0.17	0.05	0.00
ALL	9.70	5.60		3.33	0.36		4.68	0.63		1.62	0.16		0.17	0.07	
	$BaCl_2$ Acidity meq/100g														
1	72.6	40.2	3.24	20.6	3.59	0.66	39.1	0.10	0.55	17.2	1.76	0.14	0.59	1.40	0.34*
2	67.3	40.6	8.55*	19.2	2.03	0.66	39.7	4.28	0.07	18.2	1.06	0.83	1.07	0.56	0.14*
3	–	–	–	–	–	–	34.2	6.21	5.40*	15.3	0.15	2.03*	–	–	–
4	87.6	6.09	11.7*	–	–	–	43.0	4.69	3.40*	17.1	1.34	0.20	1.25	0.88	0.32*
ALL	75.9	31.3		19.9	2.90		39.6	5.40		17.3	1.54		0.93	1.10	
	KCL Extractable Al meq/100g														
1	4.73	0.55	3.85*	2.46	0.14	0.37*	3.72	0.16	0.40*	1.53	0.17	0.00	0.05	0.04	0.04*
2	6.71	1.22	1.87*	3.20	0.35	0.37*	3.92	0.40	0.24*	1.22	0.15	0.31*	0.10	0.04	0.01
3	–	–	–	–	–	–	3.63	0.24	0.49*	1.71	0.08	0.18*	–	–	–
4	14.3	3.69	5.72*	–	–	–	4.78	1.50	0.66*	1.88	0.10	0.35*	0.14	0.04	0.05*
ALL	8.58	4.77		2.83	0.46		4.12	1.00		1.53	0.29		0.10	0.06	
	Ca in 0.002M $CaCl_2$ meq/100g														
1	0.32	0.12	1.65*	0.41	0.04	0.02	0.35	0.02	0.10*	0.38	0.04	0.13*	0.55	0.07	0.13*
2	2.91	0.25	0.94*	0.45	0.03	0.02	0.51	0.04	0.06*	0.60	0.03	0.09*	0.73	0.05	0.05*
3	–	–	–	–	–	–	0.34	0.02	0.12*	0.38	0.06	0.13*	–	–	–
4	2.69	0.07	0.72*	–	–	–	0.51	0.06	0.05*	0.63	0.02	0.13*	0.80	0.03	0.12*
ALL	1.97	1.23		0.43	0.04		0.45	0.09		0.51	0.12		0.68	0.13	
	Mg in 0.002M $CaCl_2$ meq/100g														
1	0.10	0.02	0.14*	0.10	0.07	0.02	0.03	0.01	0.00	0.03	0.00	0.01	0.01	0.00	0.01
2	0.25	0.10	0.01	0.14	0.01	0.02	0.05	0.01	0.01	0.04	0.01	0.01	0.01	0.00	0.01
3	–	–	–	–	–	–	0.03	0.00	0.01	0.03	0.01	0.00	–	–	–
4	0.36	0.01	0.12*	–	–	–	0.04	0.01	0.00	0.04	0.01	0.00	0.03	0.05	0.01
ALL	0.23	0.12		0.12	0.05		0.04	0.01		0.03	0.01		0.02	0.03	
	K in 0.002M $CaCl_2$ meq/100g														
1	0.06	0.00	0.10*	0.06	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
2	0.19	0.06	0.03	0.06	0.01	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
3	–	–	–	–	–	–	0.01	0.00	0.00	0.01	0.00	0.00	–	–	–
4	0.24	0.02	0.07*	–	–	–	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
ALL	0.16	0.08		0.06	0.01		0.01	0.00		0.01	0.00		0.01	0.00	
	Na in 0.002M $CaCl_2$ meq/100g														
1	0.07	0.01	0.05*	0.03	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
2	0.13	0.06	0.01	0.03	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
3	–	–	–	–	–	–	0.01	0.00	0.00	0.02	0.01	0.00	–	–	–
4	0.17	0.00	0.05*	–	–	–	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
ALL	0.12	0.05		0.03	0.00		0.02	0.00		0.02	0.00		0.00	0.00	

(continued)

Appendix F. Continued

Lab	Audit Sample[a]														
	Oa			A			Ba			Bw			C		
	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d
Fe in 0.002M $CaCl_2$ meq/100g															
1	0.01	0.00	0.02	0.02	0.01	0.00	0.03	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.00
2	0.03	0.01	0.01	0.02	0.01	0.00	0.06	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
3	–	–	–	–	–	–	0.04	0.01	0.00	0.00	0.00	0.00	–	–	–
4	0.04	0.01	0.01	–	–	–	0.04	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
ALL	0.03	0.02		0.02	0.01		0.04	0.01		0.00	0.00		0.00	0.00	
Al in 0.002M $CaCl_2$ meq/100g															
1	0.06	0.01	0.24*	0.09	0.01	0.01	0.10	0.03	0.06	0.00	0.01	0.00	0.00	0.02	0.00
2	0.33	0.10	0.03	0.08	0.01	0.01	0.17	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
3	–	–	–	–	–	–	0.14	0.02	0.02	0.00	0.00	0.00	–	–	–
4	0.51	0.01	0.21*	–	–	–	0.19	0.03	0.03	0.01	0.00	0.01	0.01	0.00	0.00
ALL	0.30	0.20		0.09	0.01		0.16	0.04		0.00	0.01		0.00	0.01	
Fe in Pyrophosphate % dry wt															
1	0.16	0.00	0.01	0.68	0.08	0.03	0.63	0.06	0.01	0.82	0.08	0.01	0.04	0.01	0.00
2	0.23	0.13	0.05*	0.62	0.06	0.03	0.61	0.08	0.03	0.81	0.15	0.01	0.03	0.01	0.00
3	–	–	–	–	–	–	0.65	0.09	0.01	0.95	0.02	0.14*	–	–	–
4	0.14	0.01	0.04*	–	–	–	0.67	0.06	0.03	0.73	0.06	0.07*	0.04	0.01	0.00
ALL	0.16	0.08		0.65	0.07		0.64	0.07		0.80	0.11		0.04	0.01	
Al in Pyrophosphate % dry wt															
1	0.52	0.03	0.01	0.77	0.14	0.05	0.78	0.09	0.06*	0.62	0.10	0.04*	0.06	0.01	0.00
2	0.60	0.26	0.07*	0.66	0.07	0.05	0.84	0.05	0.00	0.55	0.06	0.03	0.05	0.01	0.01
3	–	–	–	–	–	–	0.83	0.10	0.01	0.58	0.02	0.00	–	–	–
4	0.47	0.01	0.06*	–	–	–	0.88	0.12	0.03	0.54	0.09	0.04	0.06	0.01	0.00
ALL	0.53	0.15		0.71	0.12		0.84	0.09		0.57	0.09		0.06	0.01	
Fe in Acid Oxalate % dry wt															
1	0.17	0.01	0.02*	0.39	0.03	0.04*	0.79	0.07	0.22*	1.01	0.18	0.02	0.06	0.01	0.02*
2	0.21	0.03	0.02*	0.48	0.02	0.04*	1.07	0.16	0.06*	1.09	0.18	0.06*	0.10	0.07	0.03*
3	–	–	–	–	–	–	1.10	0.27	0.10*	1.05	0.07	0.02	–	–	–
4	0.18	0.01	0.01	–	–	–	0.97	0.29	0.03	0.97	0.09	0.06*	0.08	0.10	0.00
ALL	0.18	0.03		0.44	0.05		1.00	0.24		1.03	0.16		0.07	0.07	
Al in Acid Oxalate % dry wt															
1	0.41	0.04	0.08*	0.38	0.03	0.08*	1.01	0.09	0.11*	0.90	0.09	0.01	0.08	0.02	0.00
2	0.56	0.08	0.07*	0.55	0.03	0.08*	1.28	0.09	0.16*	0.93	0.10	0.02	0.08	0.02	0.00
3	–	–	–	–	–	–	0.98	0.07	0.14*	0.86	0.05	0.05	–	–	–
4	0.50	0.05	0.01	–	–	–	1.08	0.12	0.04	0.92	0.04	0.01	0.08	0.02	0.00
ALL	0.49	0.08		0.46	0.09		1.12	0.15		0.91	0.08		0.08	0.02	
Fe in Citrate Dithionite % dry wt															
1	0.15	0.02	0.00	1.74	0.24	0.28*	1.03	0.03	0.02	1.50	0.15	0.05	0.18	0.04	0.01
2	0.14	0.01	0.01	1.17	0.72	0.28*	0.98	0.17	0.07*	1.43	0.25	0.12*	0.17	0.05	0.00
3	–	–	–	–	–	–	1.26	0.21	0.21*	2.15	0.00	0.60*	–	–	–
4	0.17	0.00	0.01	–	–	–	1.01	0.11	0.04	1.61	0.08	0.05	0.15	0.02	0.02
ALL	0.15	0.02		1.45	0.59		1.06	0.18		1.55	0.25		0.17	0.03	
Al in Citrate Dithionite % dry wt															
1	0.39	0.03	0.04*	0.46	0.04	0.01	0.83	0.02	0.07*	0.52	0.06	0.10*	0.05	0.01	0.01
2	0.44	0.03	0.01	0.44	0.14	0.01	0.85	0.16	0.06*	0.68	0.11	0.06*	0.07	0.02	0.01
3	–	–	–	–	–	–	0.92	0.19	0.01	0.86	0.03	0.24*	–	–	–
4	0.46	0.01	0.03*	–	–	–	0.99	0.08	0.08*	0.62	0.04	0.00	0.06	0.01	0.00
ALL	0.43	0.04		0.45	0.10		0.91	0.14		0.62	0.12		0.06	0.01	

(continued)

Appendix F. Continued

Lab	Audit Sample[a]														
	Oa			A			Bs			Bw			C		
	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d
Sulfate in H_2O mg S/kg															
1	52.0	3.94	1.30	31.1	3.15	0.88	7.25	0.31	1.38*	20.1	1.26	0.38	2.81	0.58	0.36*
2	48.5	3.46	2.19	32.9	2.55	0.88	9.22	1.25	0.59*	20.3	0.99	0.16	2.50	0.72	0.05
3	–	–	–	–	–	–	7.57	0.87	1.05*	21.5	0.59	1.05*	–	–	–
4	51.6	0.72	0.87	–	–	–	9.28	1.81	0.65*	20.9	1.53	0.48	2.00	0.71	0.46*
ALL	50.7	3.21		32.0	2.92		8.63	1.54		20.5	1.24		2.45	0.73	
Sulfate in PO_4 mg S/kg															
1	63.4	5.17	6.60*	78.3	4.01	1.50	33.8	6.99	6.50*	101	3.51	4.70	4.13	0.61	0.77*
2	50.4	2.09	6.34*	75.3	11.5	1.50	26.8	3.91	0.57	108	3.22	2.00	3.27	1.25	0.09
3	–	–	–	–	–	–	27.7	2.99	0.34	111	1.80	5.30	–	–	–
4	56.5	4.19	0.29	–	–	–	25.1	3.51	2.24*	109	7.86	3.40	2.49	1.02	0.87*
ALL	56.8	6.63		76.8	8.45		27.3	4.78		106	5.91		3.36	1.16	
Sulfate 0 mg S/L															
1	11.9	0.21	0.56	4.21	0.19	0.02	1.22	0.09	0.12*	2.03	0.06	0.03	0.50	0.07	0.01
2	11.2	0.19	0.14	4.16	0.25	0.02	1.38	0.11	0.04	2.05	0.18	0.05	0.55	0.13	0.06*
3	–	–	–	–	–	–	1.28	0.14	0.06	2.04	0.04	0.04	–	–	–
4	10.9	0.98	0.42	–	–	–	1.39	0.31	0.05	1.87	0.16	0.13*	0.44	0.08	0.05*
ALL	11.3	0.69		4.19	0.22		1.34	0.21		2.00	0.14		0.49	0.09	
Sulfate 2 mg S/L															
1	14.5	0.23	0.97*	5.43	0.24	0.18	2.94	0.19	0.07	2.98	0.16	0.05	2.48	0.16	0.09
2	13.6	0.45	0.11	5.79	0.18	0.18	2.94	0.13	0.07	2.96	0.18	0.03	2.33	0.23	0.06
3	–	–	–	–	–	–	2.73	0.11	0.15	2.98	0.10	0.04	–	–	–
4	12.4	0.48	1.08*	–	–	–	2.87	0.24	0.01	2.80	0.07	0.13	2.30	0.10	0.08
ALL	13.5	0.95		5.61	0.28		2.87	0.19		2.93	0.16		2.38	0.17	
Sulfate 4 mg S/L															
1	16.2	0.12	0.51	6.72	0.24	0.29	4.24	0.15	0.07	3.77	0.30	0.09	4.42	0.19	0.10
2	16.1	0.29	0.42	7.31	0.31	0.29	4.38	0.12	0.06	4.12	0.21	0.26*	4.24	0.35	0.07
3	–	–	–	–	–	–	4.28	0.03	0.04	3.88	0.09	0.02	–	–	–
4	14.8	0.47	0.92*	–	–	–	4.31	0.16	0.01	3.66	0.25	0.20*	4.23	0.24	0.08
ALL	15.7	0.74		7.02	0.41		4.32	0.13		3.86	0.30		4.31	0.26	
Sulfate 8 mg S/L															
1	19.8	0.68	0.60	9.94	0.22	0.43	7.67	0.35	0.14	6.22	0.16	0.04	8.10	0.59	0.02
2	19.7	0.84	0.49	10.80	0.28	0.43	7.47	0.23	0.07	6.58	0.21	0.40*	8.20	0.40	0.12
3	–	–	–	–	–	–	7.71	0.25	0.17	6.48	0.02	0.30	–	–	–
4	18.1	0.89	1.09*	–	–	–	7.45	0.31	0.09	5.47	0.37	0.71*	7.98	0.53	0.10
ALL	19.2	1.09		10.40	0.51		7.54	0.29		6.18	0.48		8.08	0.52	
Sulfate 16 mg S/L															
1	29.1	0.68	1.80*	16.7	0.67	0.73	14.2	0.48	0.46	11.1	0.74	0.24	16.00	0.69	0.02
2	26.4	0.33	0.88	18.2	1.17	0.73	15.1	0.79	0.43	12.0	0.57	0.68*	16.30	0.71	0.24
3	–	–	–	–	–	–	14.8	0.14	0.08	11.9	0.20	0.62*	–	–	–
4	26.4	0.20	0.89	–	–	–	14.4	0.53	0.29	10.6	0.48	0.71*	15.90	1.42	0.12
ALL	27.3	1.37		17.5	1.19		14.7	0.66		11.3	0.81		16.0	0.99	
Sulfate 32 mg S/L															
1	47.7	5.83	4.80*	30.3	2.10	0.25	28.9	1.39	0.01	23.9	1.22	0.14	31.9	1.26	0.37
2	41.1	0.58	1.79	30.8	1.33	0.25	29.0	0.25	0.08	24.1	1.67	0.36	31.5	0.98	0.03
3	–	–	–	–	–	–	29.5	0.40	0.55	24.7	0.03	0.97	–	–	–
4	39.9	1.59	3.02*	–	–	–	28.5	1.18	0.41	22.7	0.98	1.04	31.1	1.86	0.43
ALL	42.9	4.79		30.5	1.72		28.9	0.90		23.8	1.37		31.5	1.45	

(continued)

Appendix F. Continued

Lab	Audit Sample[a]														
	Oa			A			Bs			Bw			C		
	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d	Mean	SD	d
							Total Carbon % dry wt								
1	32.5	1.18	5.80*	4.57	0.29	0.19	6.08	0.28	2.08*	1.58	0.03	0.02	0.16	0.03	0.02
2	42.4	2.07	4.10*	4.95	0.51	0.19	3.88	0.33	0.12	1.53	0.05	0.02	0.13	0.01	0.02
3	–	–	–	–	–	–	3.51	0.45	0.49*	1.48	0.09	0.07	–	–	–
4	40.0	1.61	1.70	–	–	–	3.58	0.49	0.42*	1.57	0.06	0.02	0.13	0.03	0.01
ALL	38.3	4.64		4.76	0.45		4.00	0.93		1.56	0.06		0.14	0.03	
							Total Nitrogen % dry wt								
1	0.89	0.13	0.25*	0.18	0.05	0.01	0.18	0.02	0.05*	0.13	0.03	0.00	0.00	0.00	0.00
2	1.31	0.09	0.16*	0.16	0.01	0.01	0.12	0.01	0.01	0.11	0.00	0.01	0.00	0.00	0.00
3	–	–	–	–	–	–	0.12	0.01	0.01	0.11	0.01	0.01	–	–	–
4	1.23	0.05	0.09*	–	–	–	0.12	0.01	0.01	0.13	0.01	0.01	0.00	0.00	0.00
ALL	1.14	0.21		0.17	0.04		0.13	0.02		0.12	0.02		0.00	0.00	
							Total Sulfur % dry wt								
1	0.243	0.01	0.011	0.024	0.01	0.003	0.030	0.00	0.012	0.020	0.01	0.001	0.002	0.00	0.001
2	0.252	0.02	0.019*	0.030	0.00	0.003	0.019	0.00	0.001	0.017	0.01	0.002	0.006	0.00	0.005
3	–	–	–	–	–	–	0.017	0.01	0.001	0.020	0.00	0.001	–	–	–
4	0.201	0.01	0.031*	–	–	–	0.012	0.01	0.006	0.021	0.00	0.002	0.002	0.00	0.001
ALL	0.232	0.03		0.027	0.01		0.018	0.01		0.019	0.01		0.001	0.00	

[a] SD is standard deviation; d is difference from the interlaboratory mean.

[b] * Relative difference greater than 5 percent.

[c] – Not analyzed by laboratory.

Appendix G

Range and Frequency Distributions

Appendix G consists of figures displaying histograms showing the range and frequency distribution of the routine samples (RS), the field duplicates (FD), the preparation duplicates (PD), and the natural audit samples (AS). Supplemental information relating to these plots can be found under "Representativeness" in Sections 2 and 3 of the report. Histograms are presented for each of the 51 analytical parameters in the order described in Table 1-1 of Section 1 of the report.

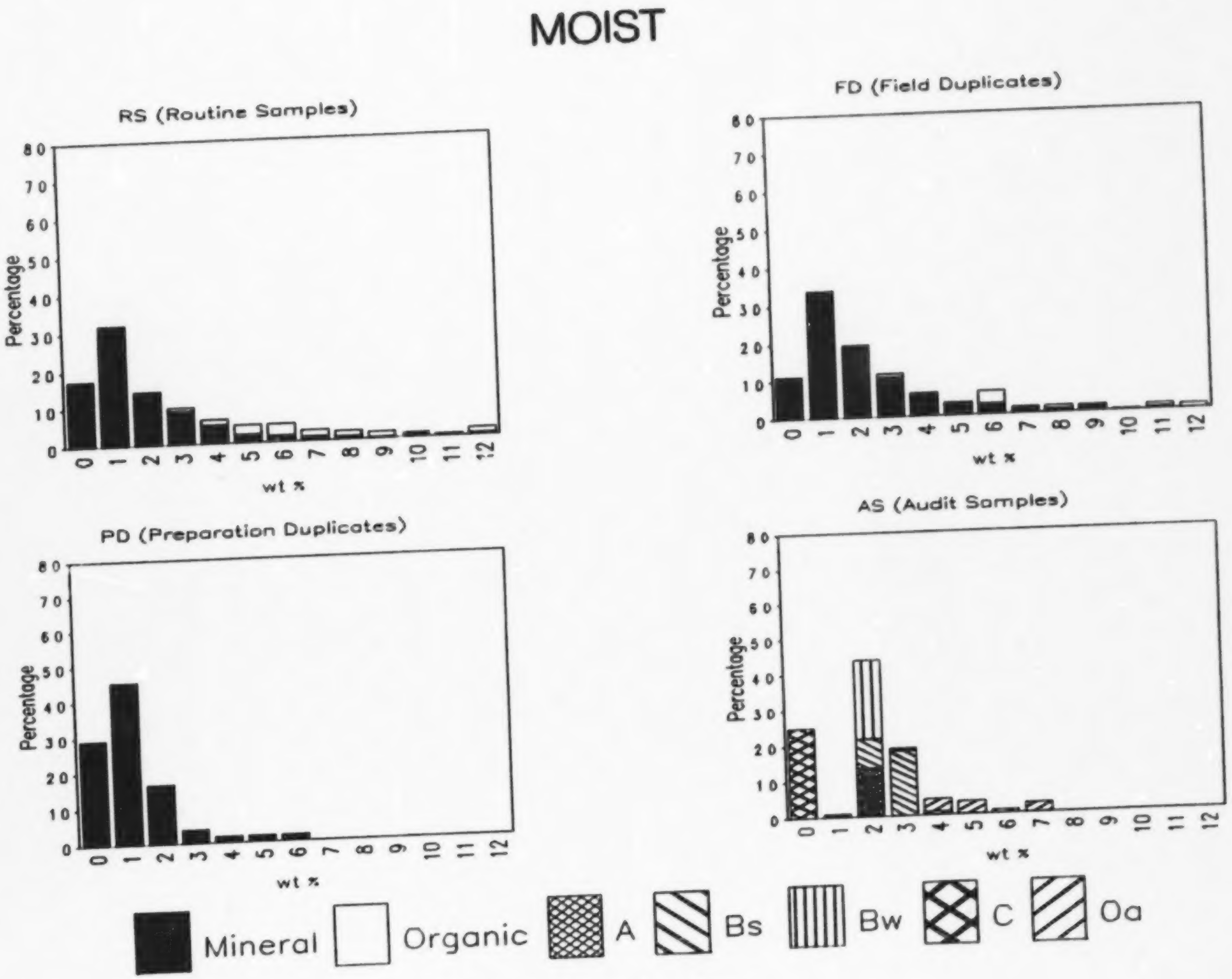


Figure G-1. Range and frequency distribution for air-dry moisture.

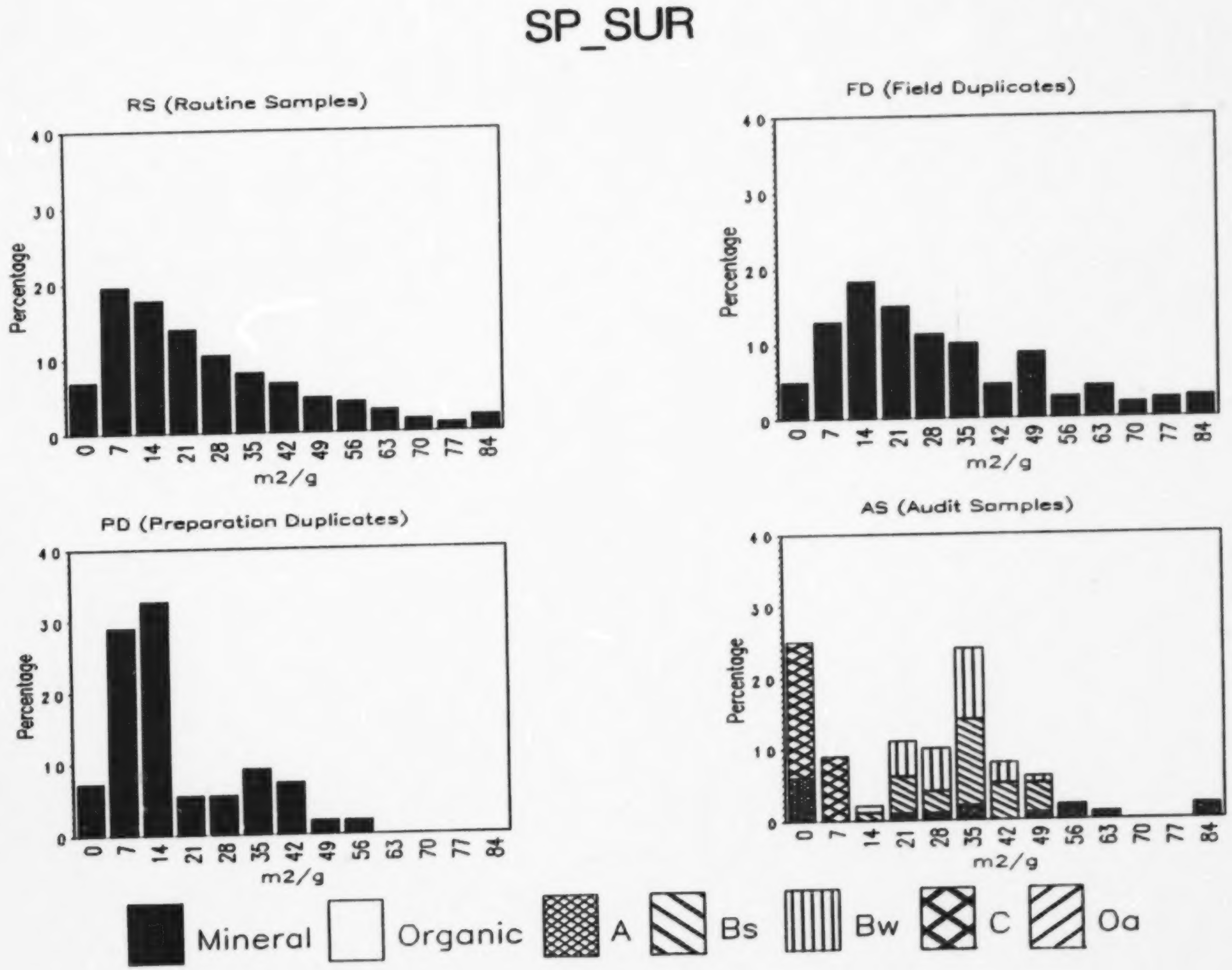


Figure G-2. Range and frequency distribution for specific surface.

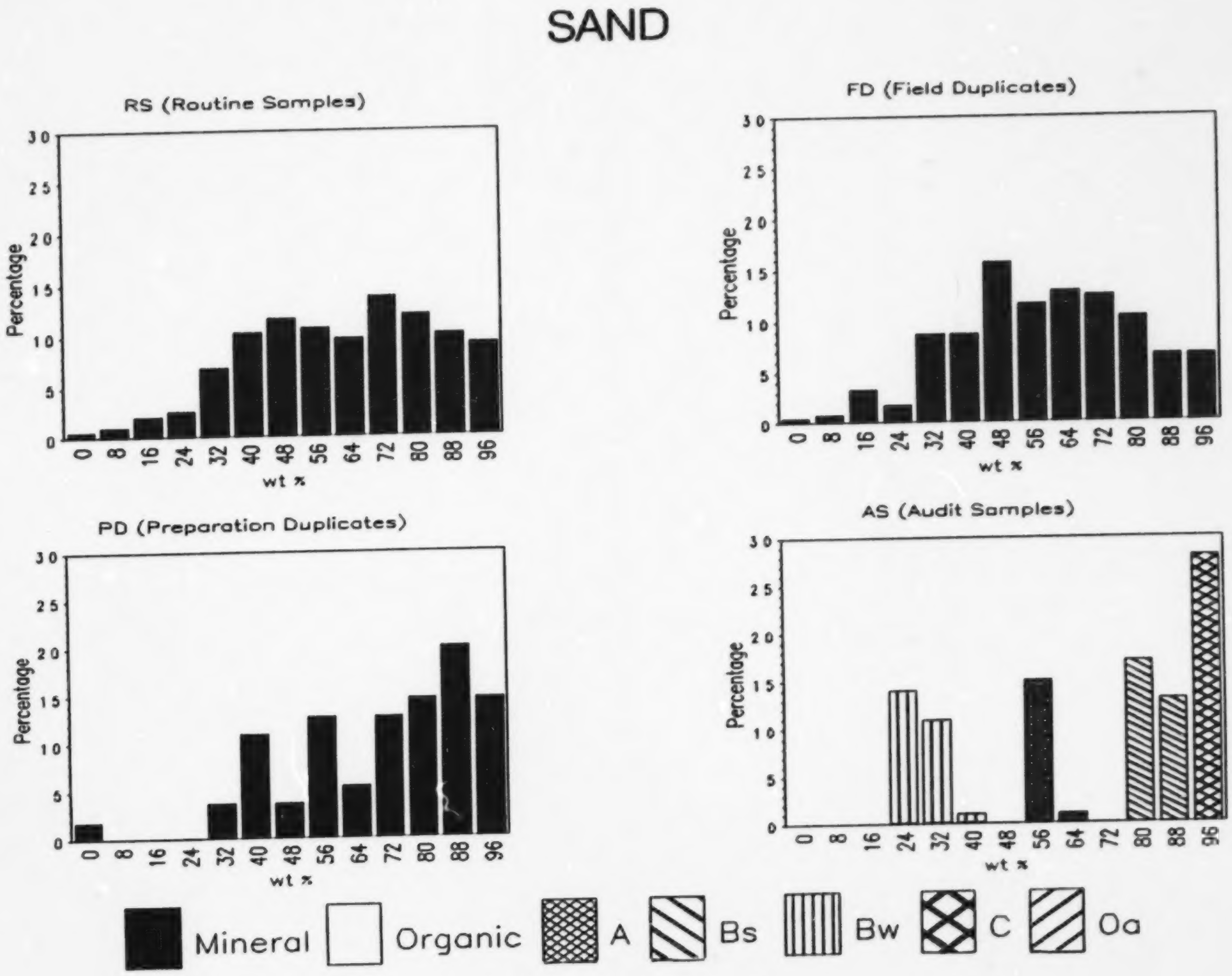


Figure G-3. Range and frequency distribution for total sand.

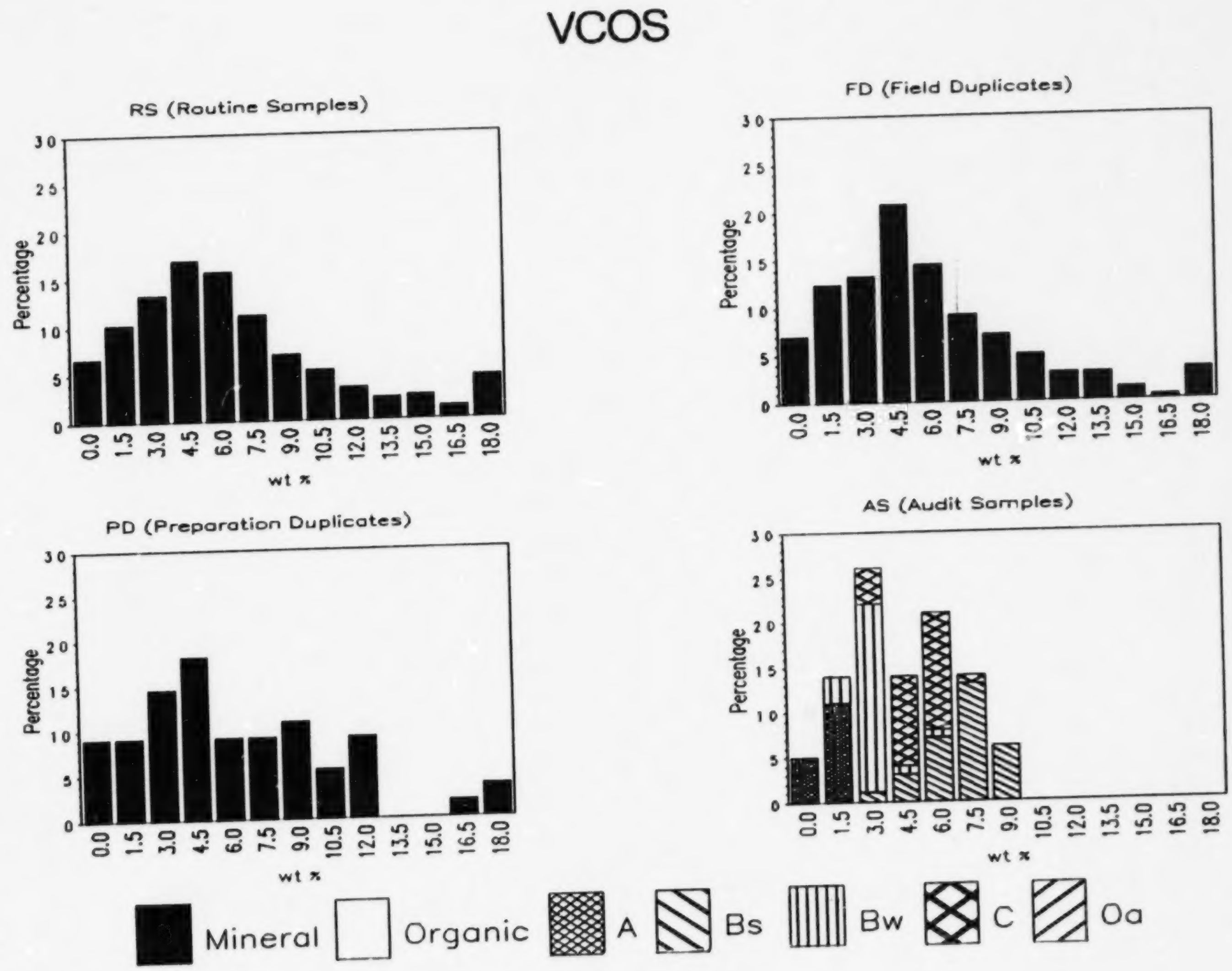


Figure G-4. Range and frequency distribution for very coarse sand.

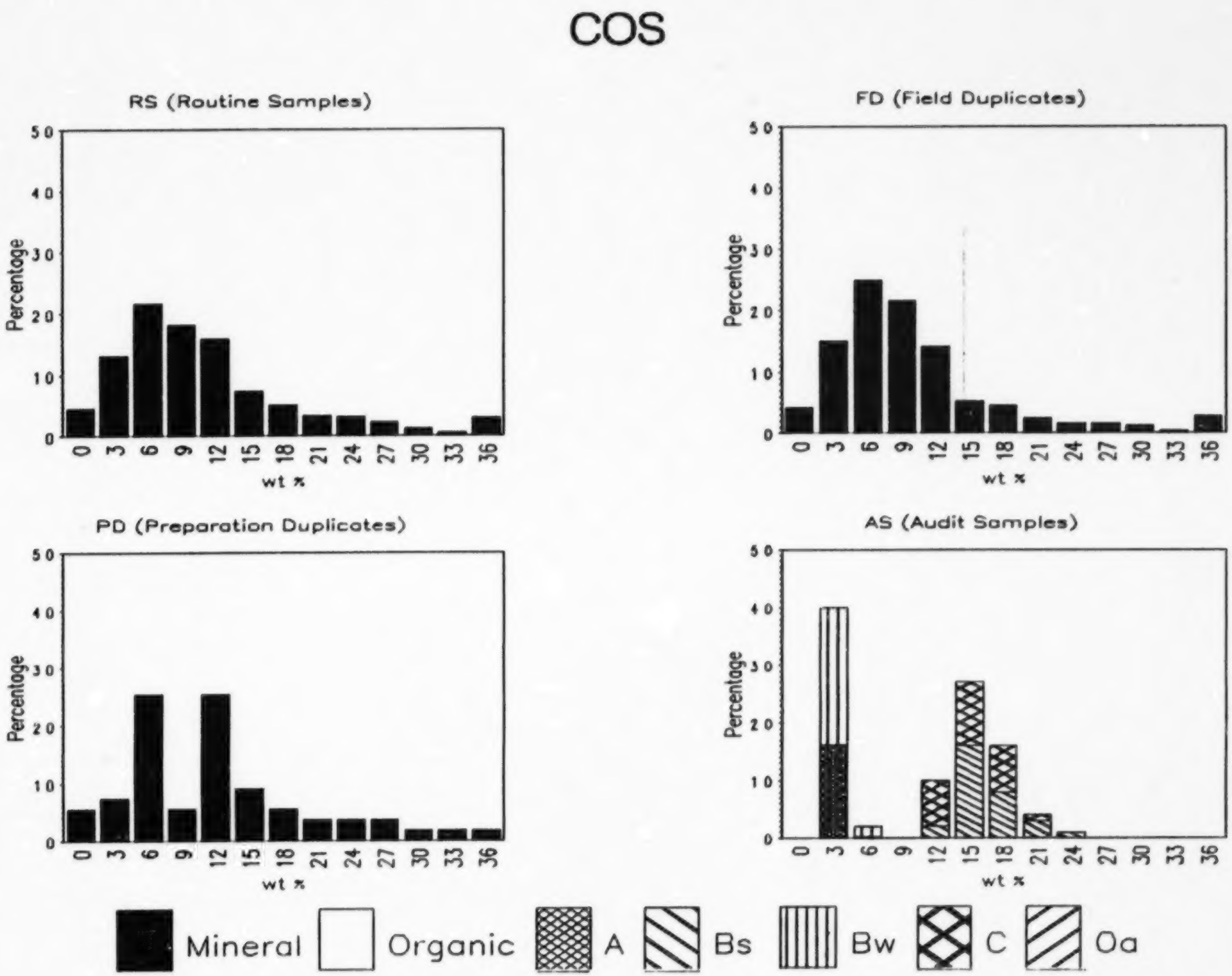


Figure G-5. Range and frequency distribution for coarse sand.

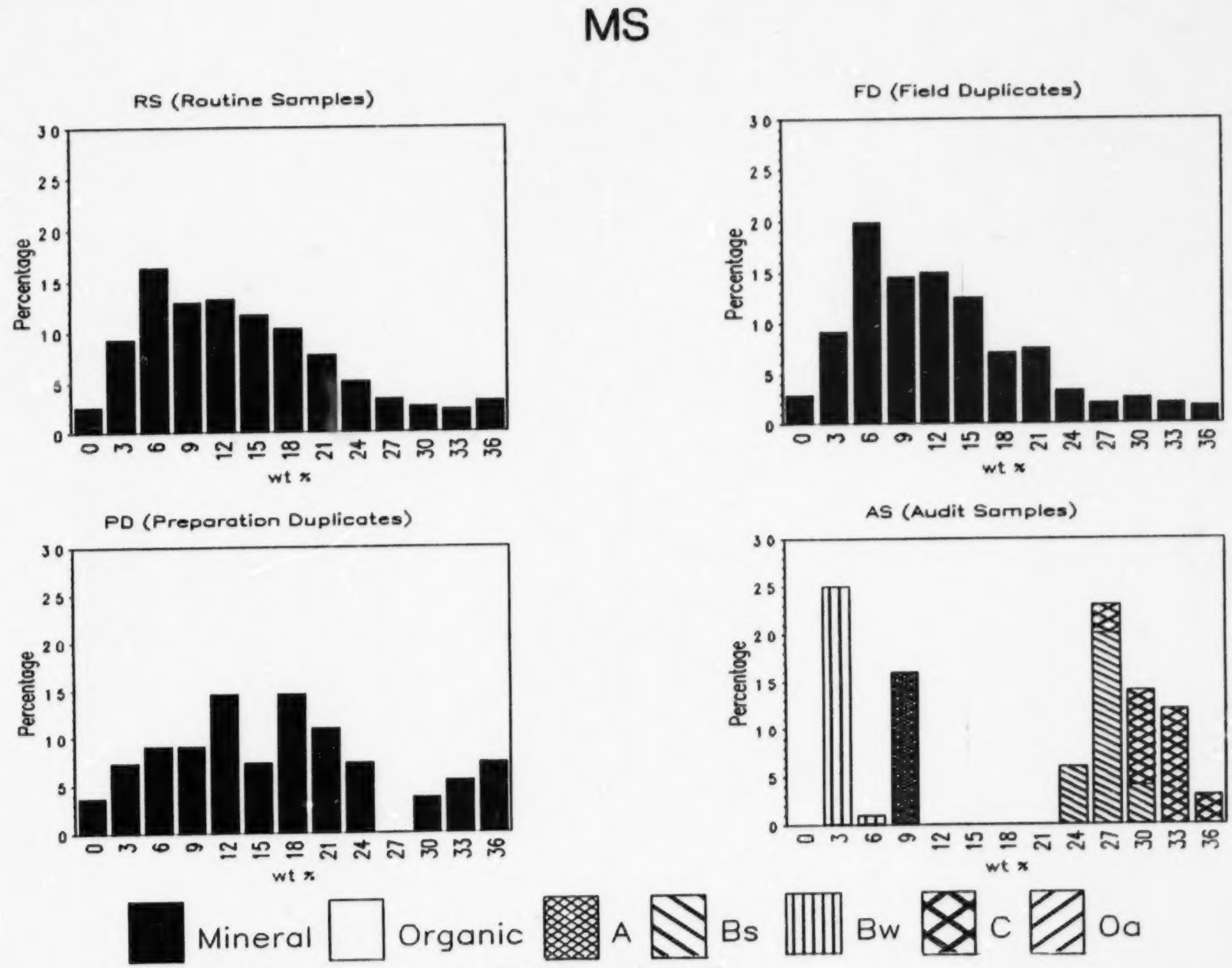


Figure G-6. Range and frequency distribution for medium sand.

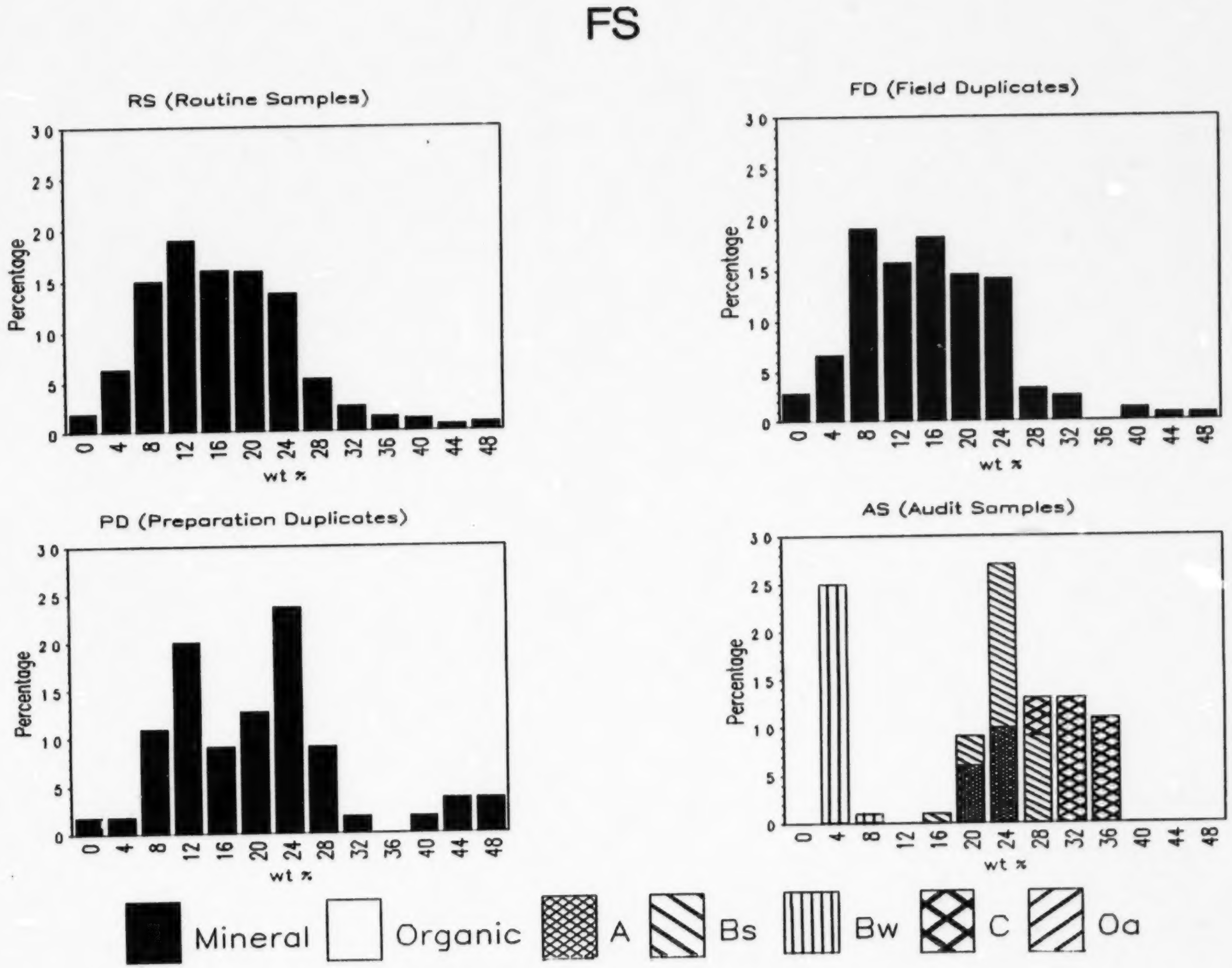


Figure G-7. Range and frequency distribution for fine sand.

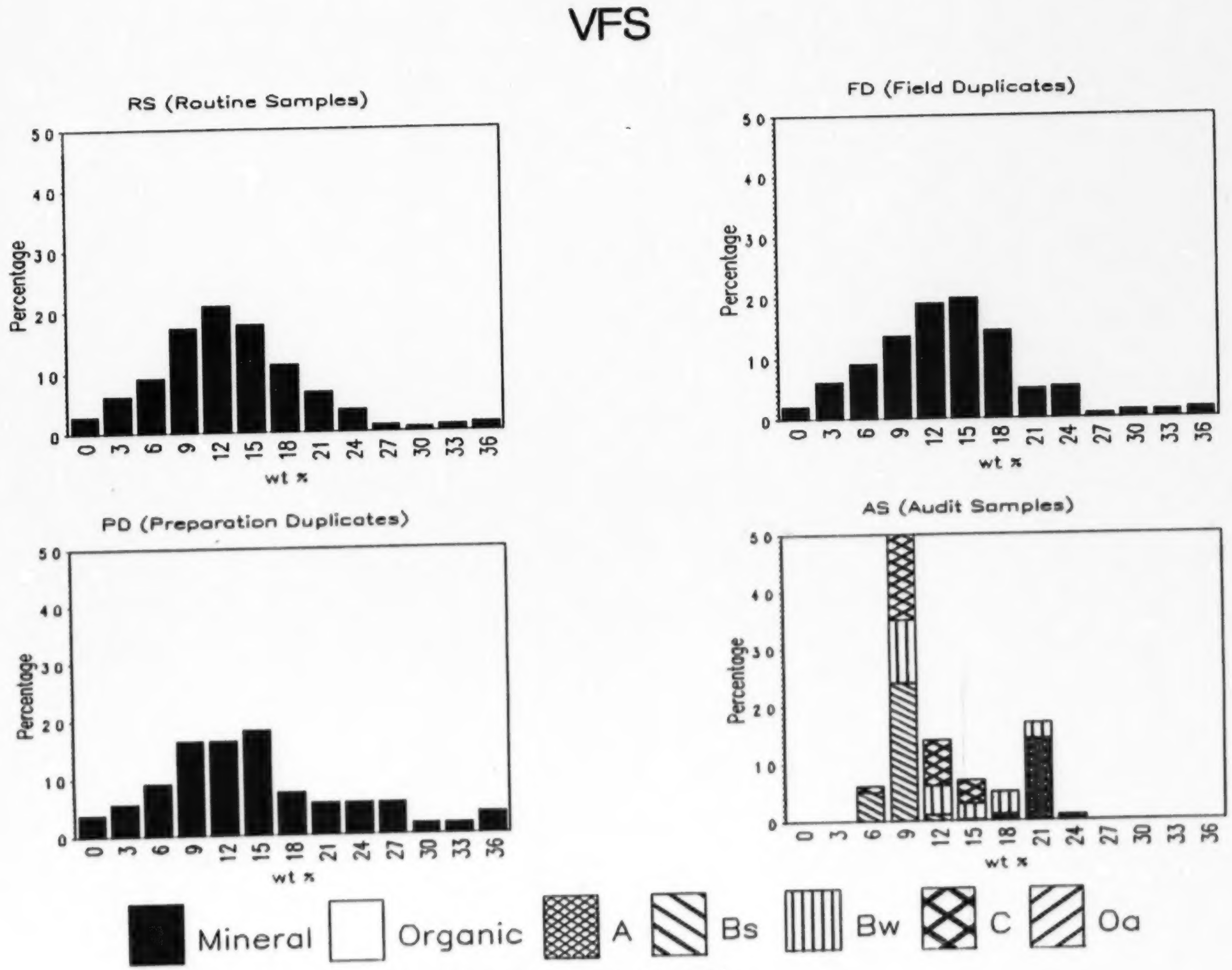


Figure G-8. Range and frequency distribution for very fine sand.

SILT

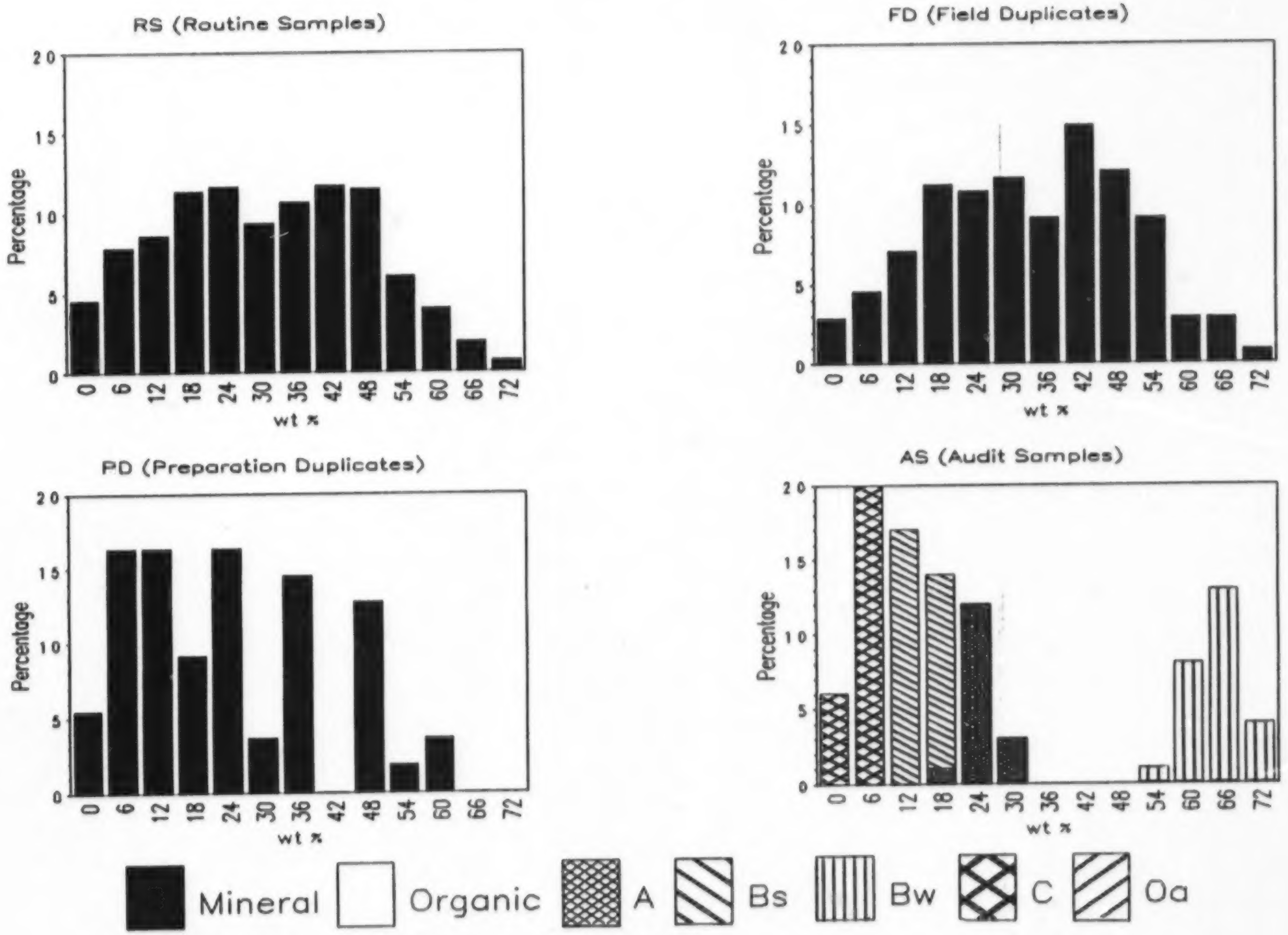


Figure G-9. Range and frequency distribution for total silt.

COSI

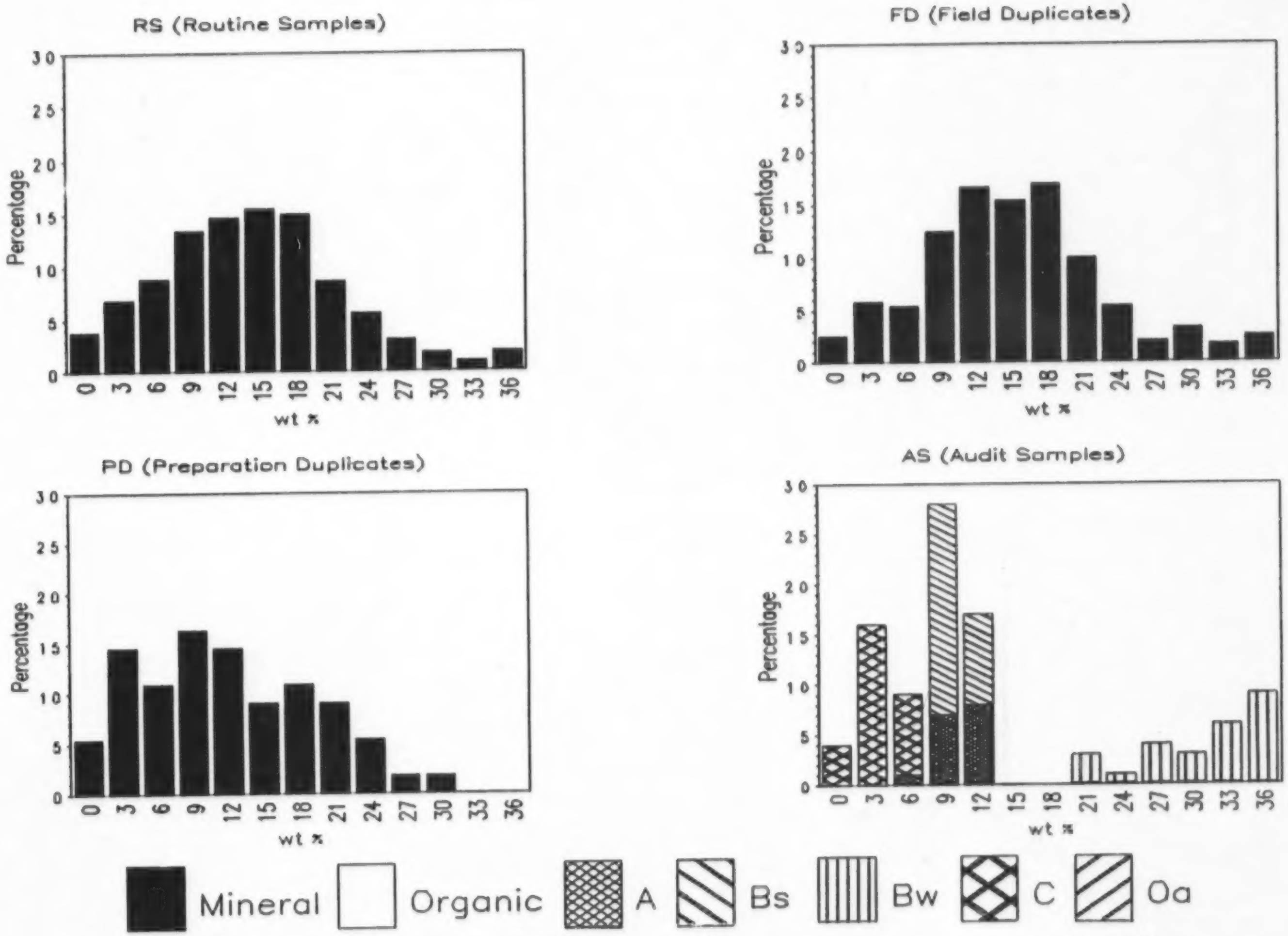


Figure G-10. Range and frequency distribution for coarse silt.

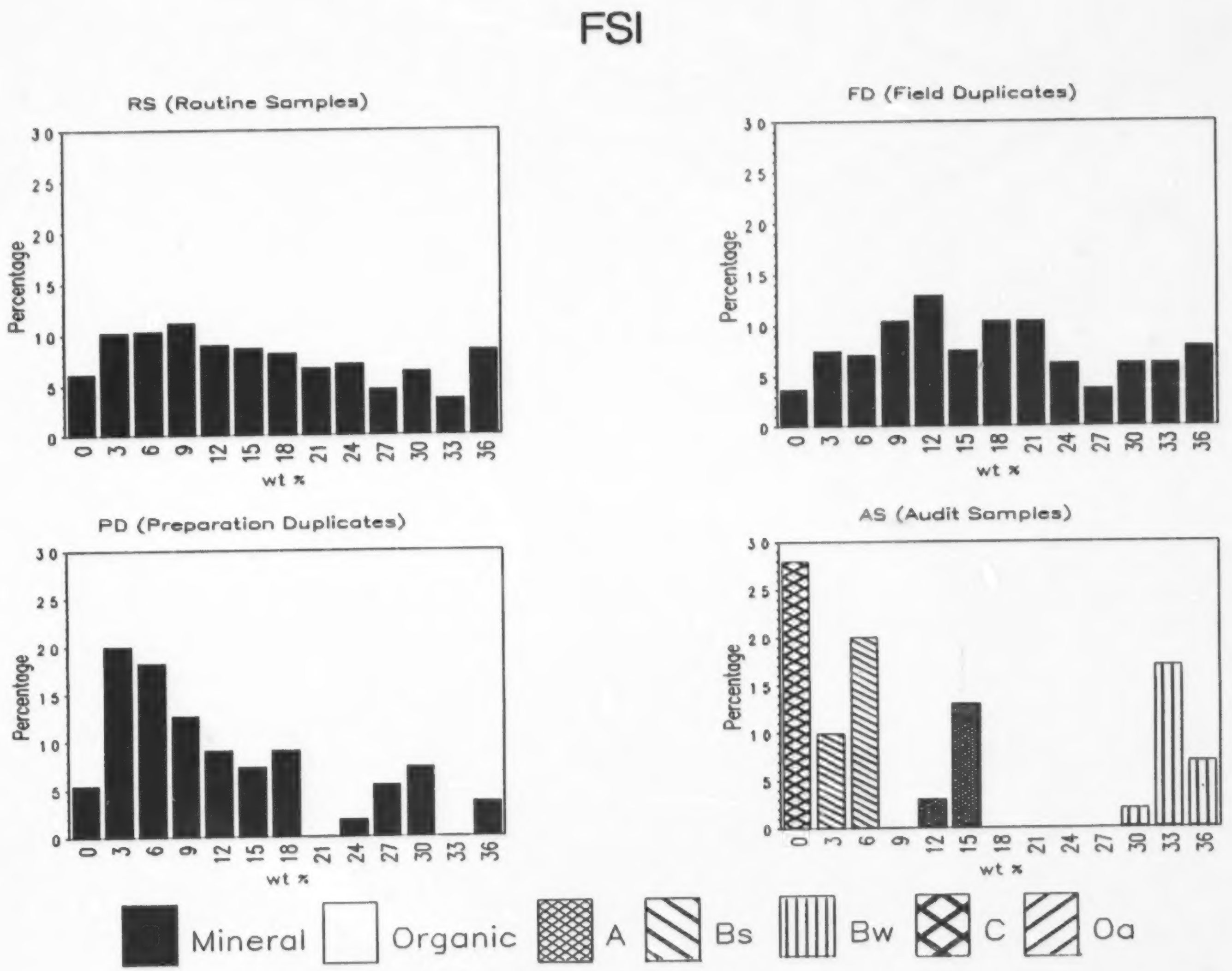


Figure G-11. Range and frequency distribution for fine silt.

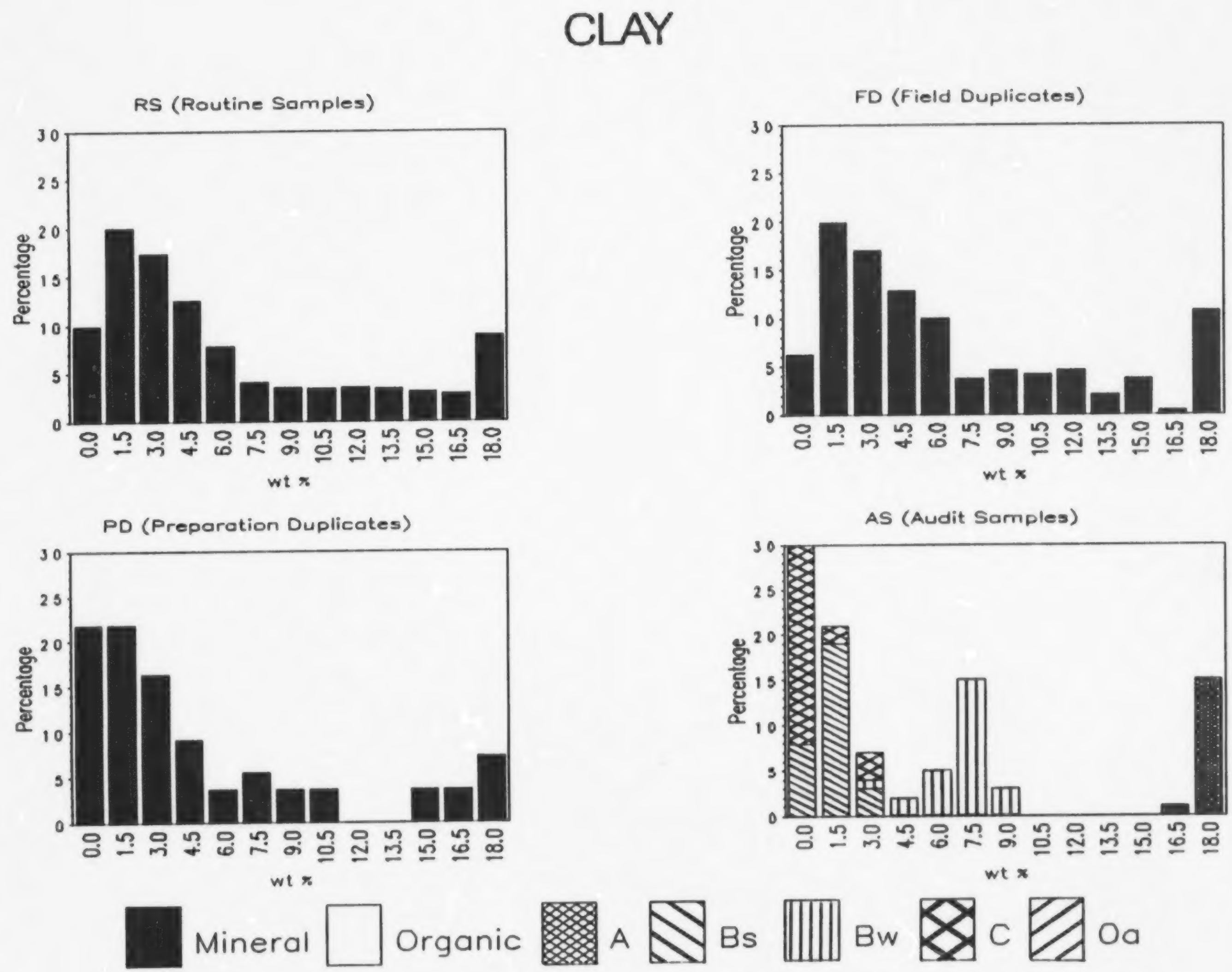


Figure G-12. Range and frequency distribution for total clay.

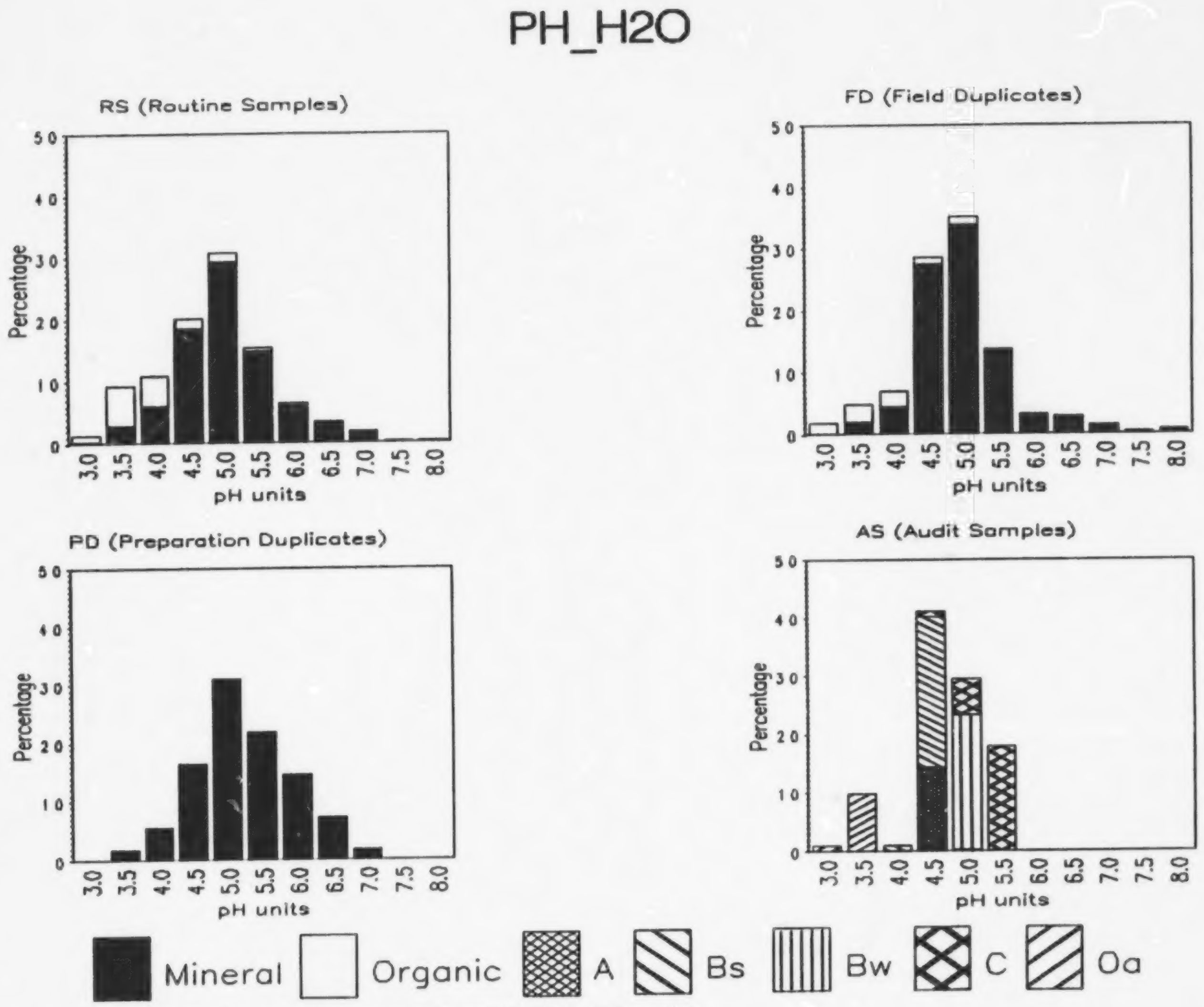


Figure G-13. Range and frequency distribution for pH in water.

PH_002M

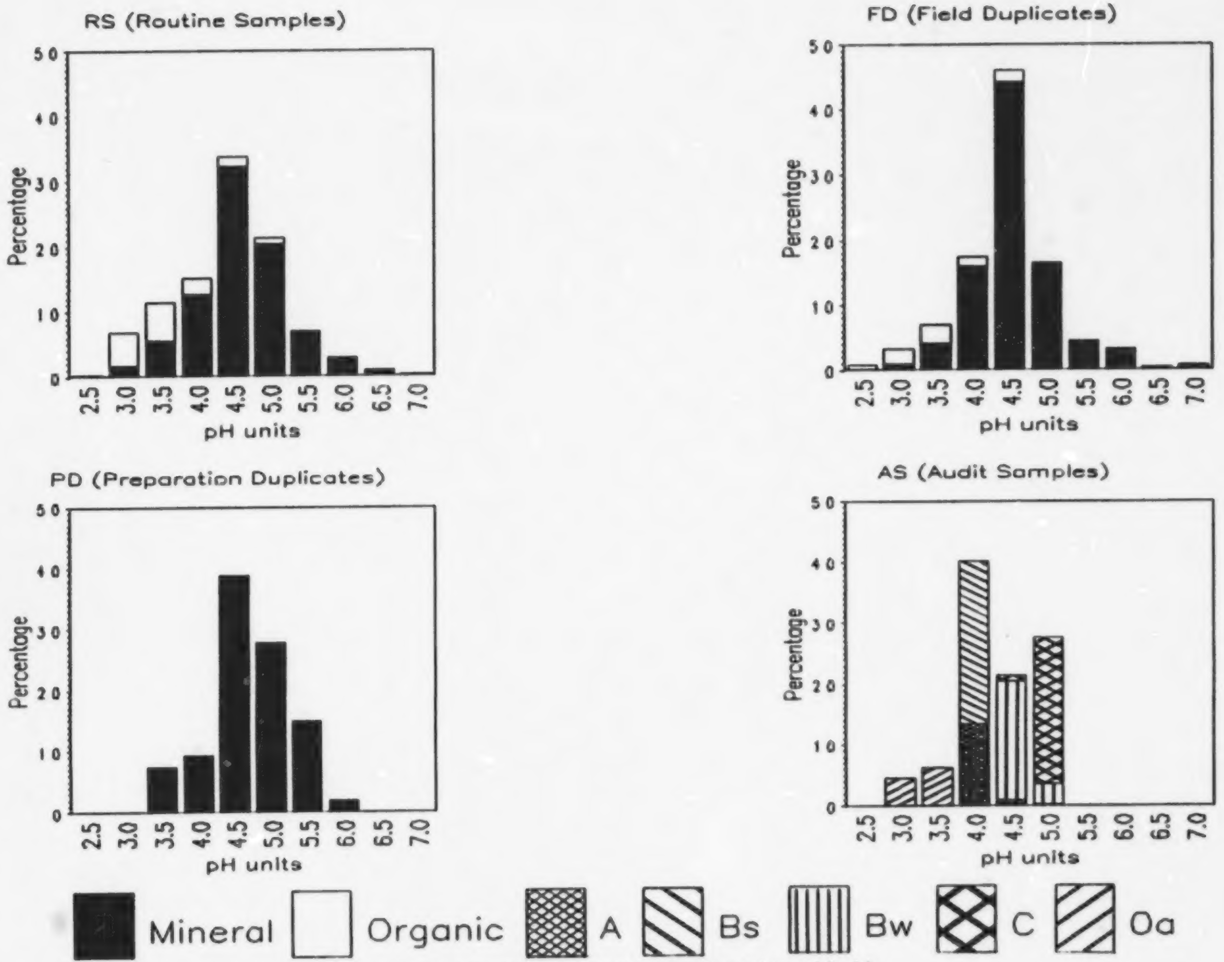


Figure G-14. Range and frequency distribution for pH in 0.002M calcium chloride.

PH_01M

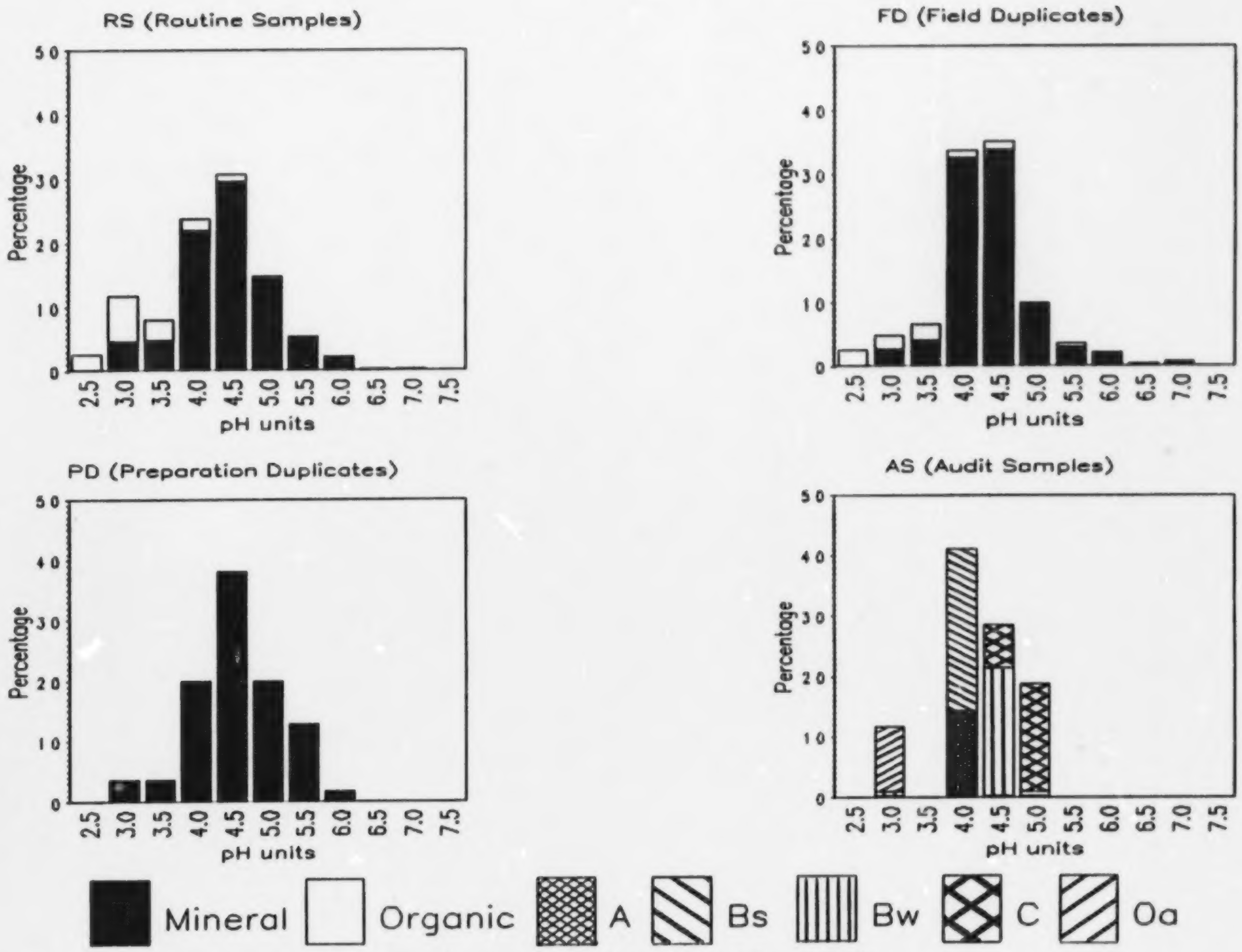


Figure G-15. Range and frequency distribution for pH in 0.01M calcium chloride.

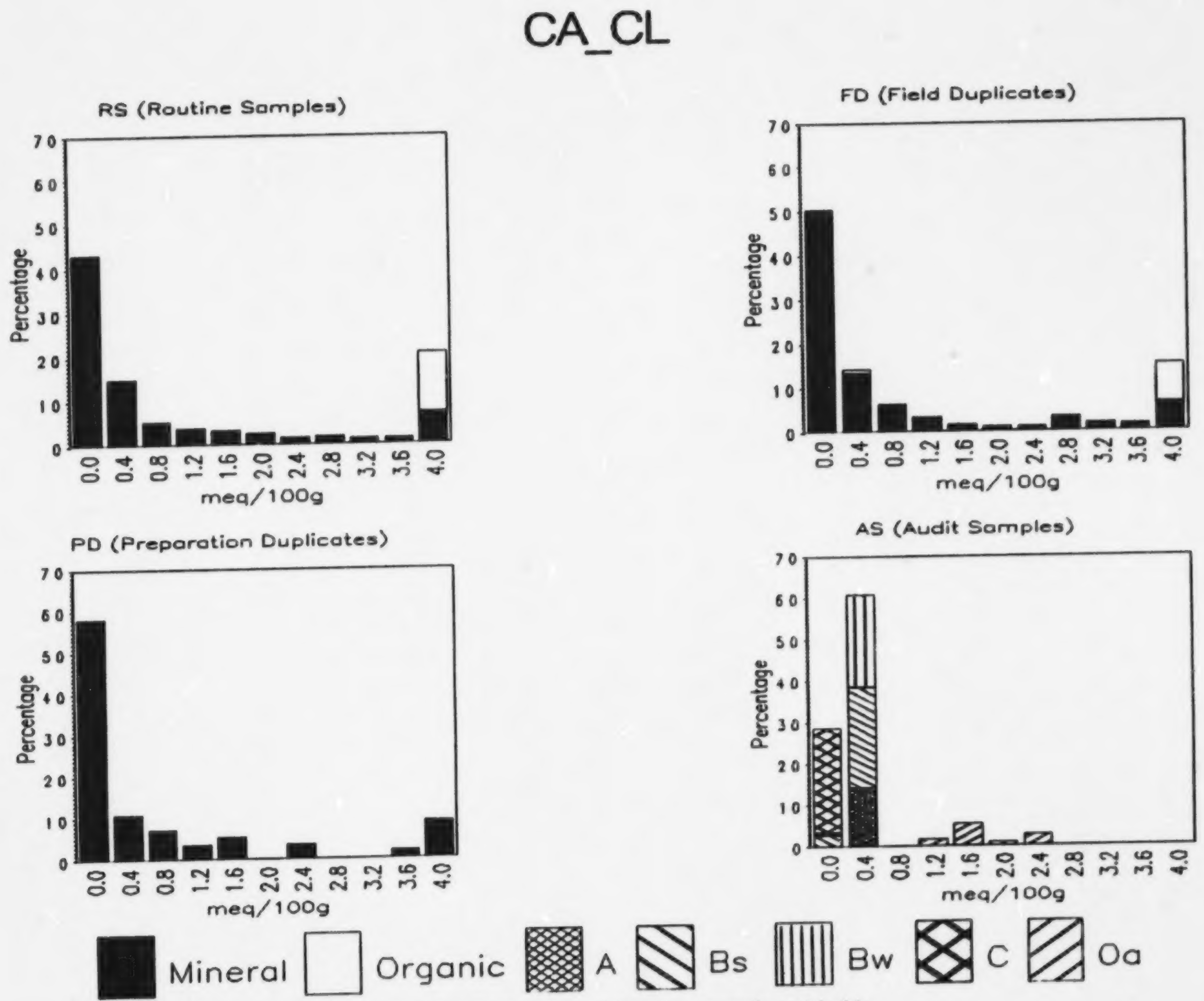


Figure G-16. Range and frequency distribution for calcium in ammonium chloride.

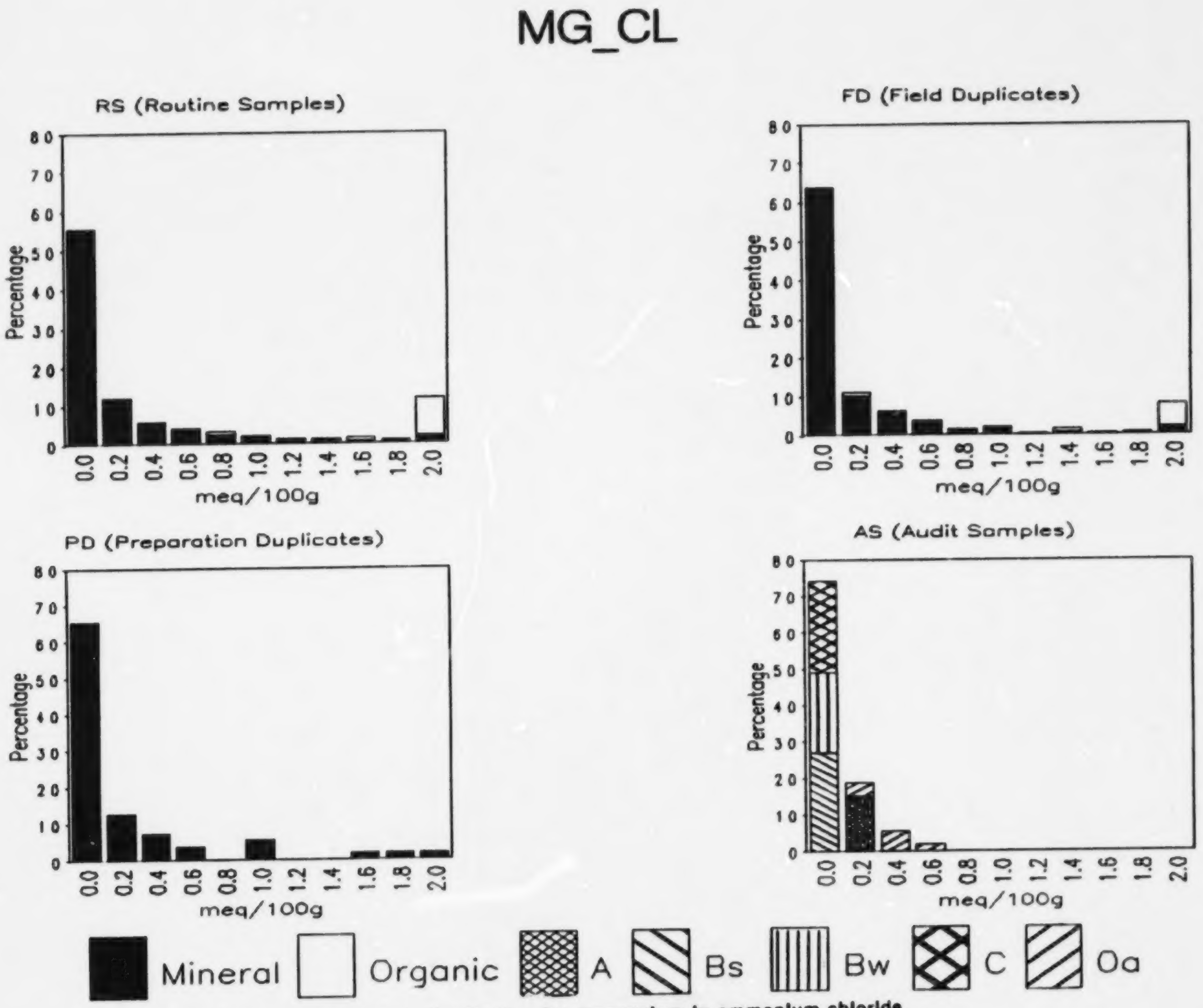


Figure G-17. Range and frequency distribution for magnesium in ammonium chloride.

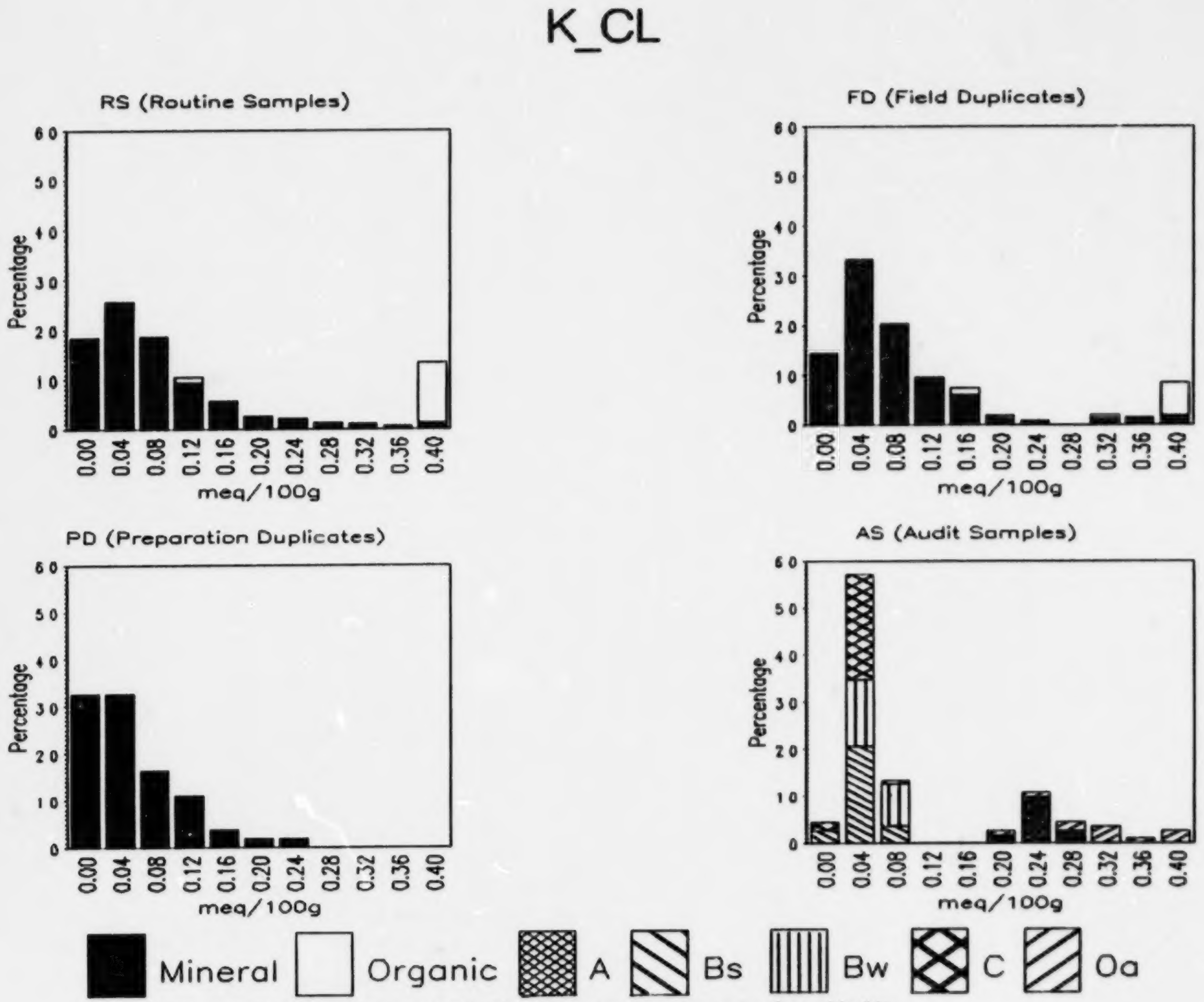


Figure G-18. Range and frequency distribution for potassium in ammonium chloride.

NA_CL

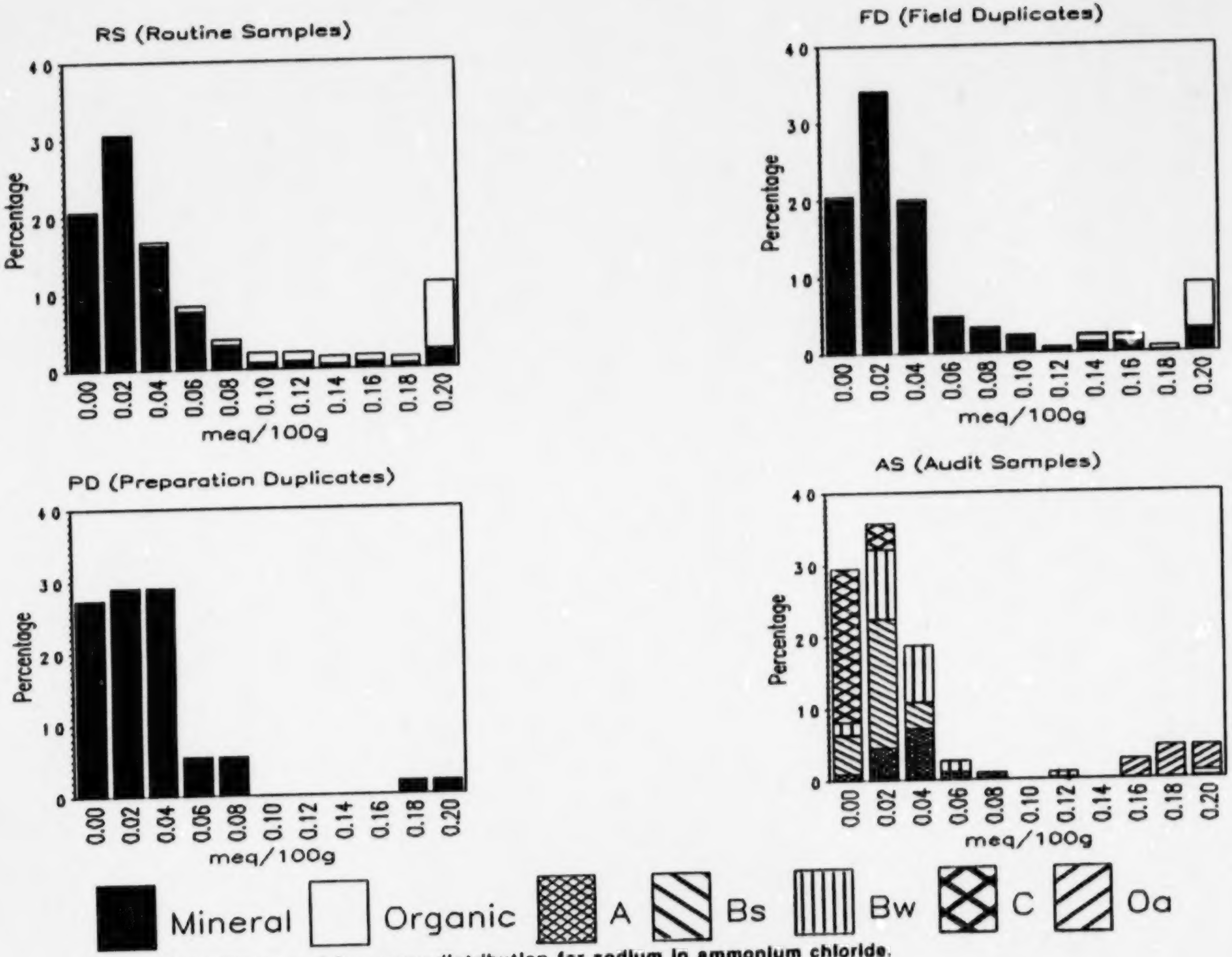


Figure G-19. Range and frequency distribution for sodium in ammonium chloride.

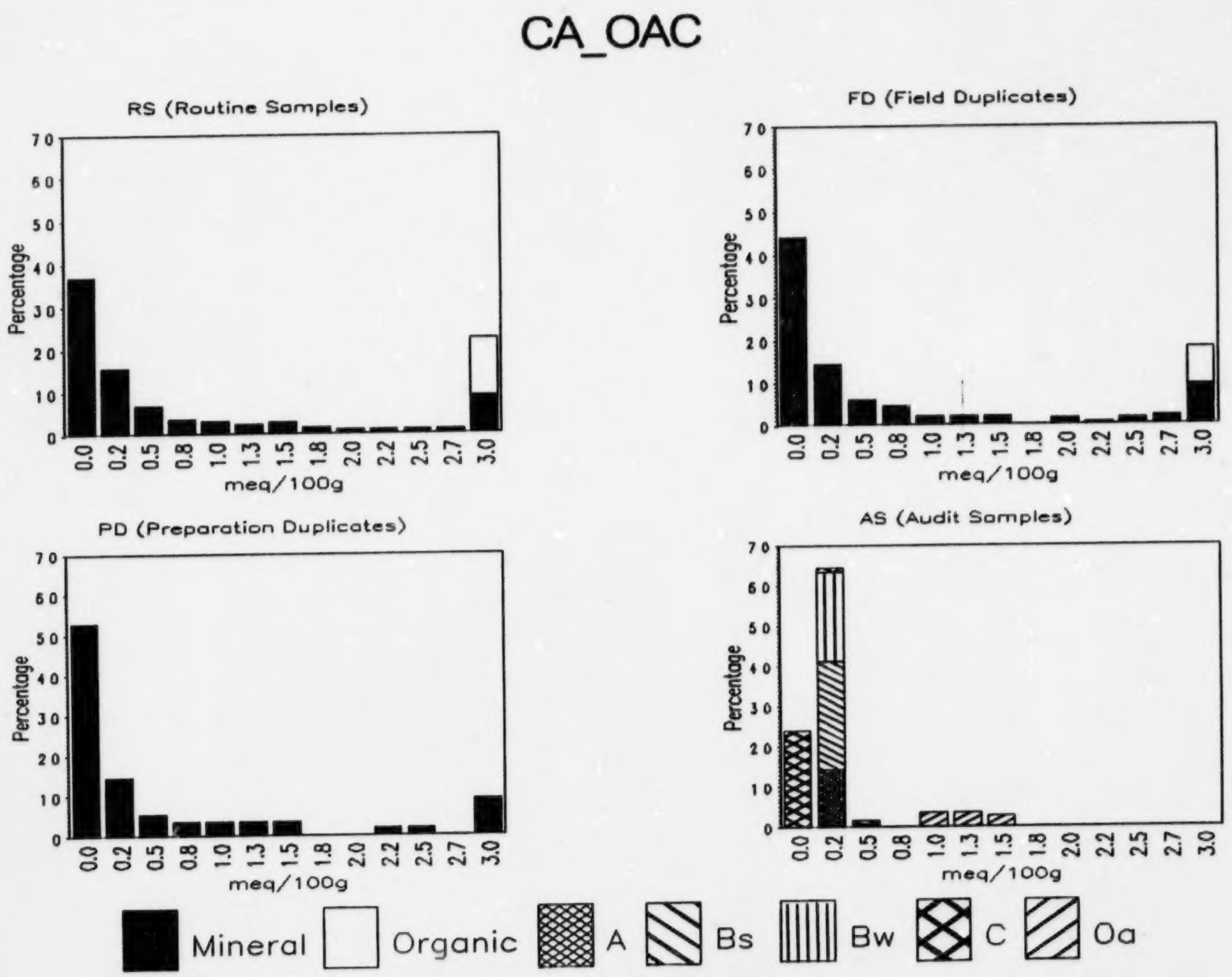


Figure G-20. Range and frequency distribution for calcium in ammonium acetate.

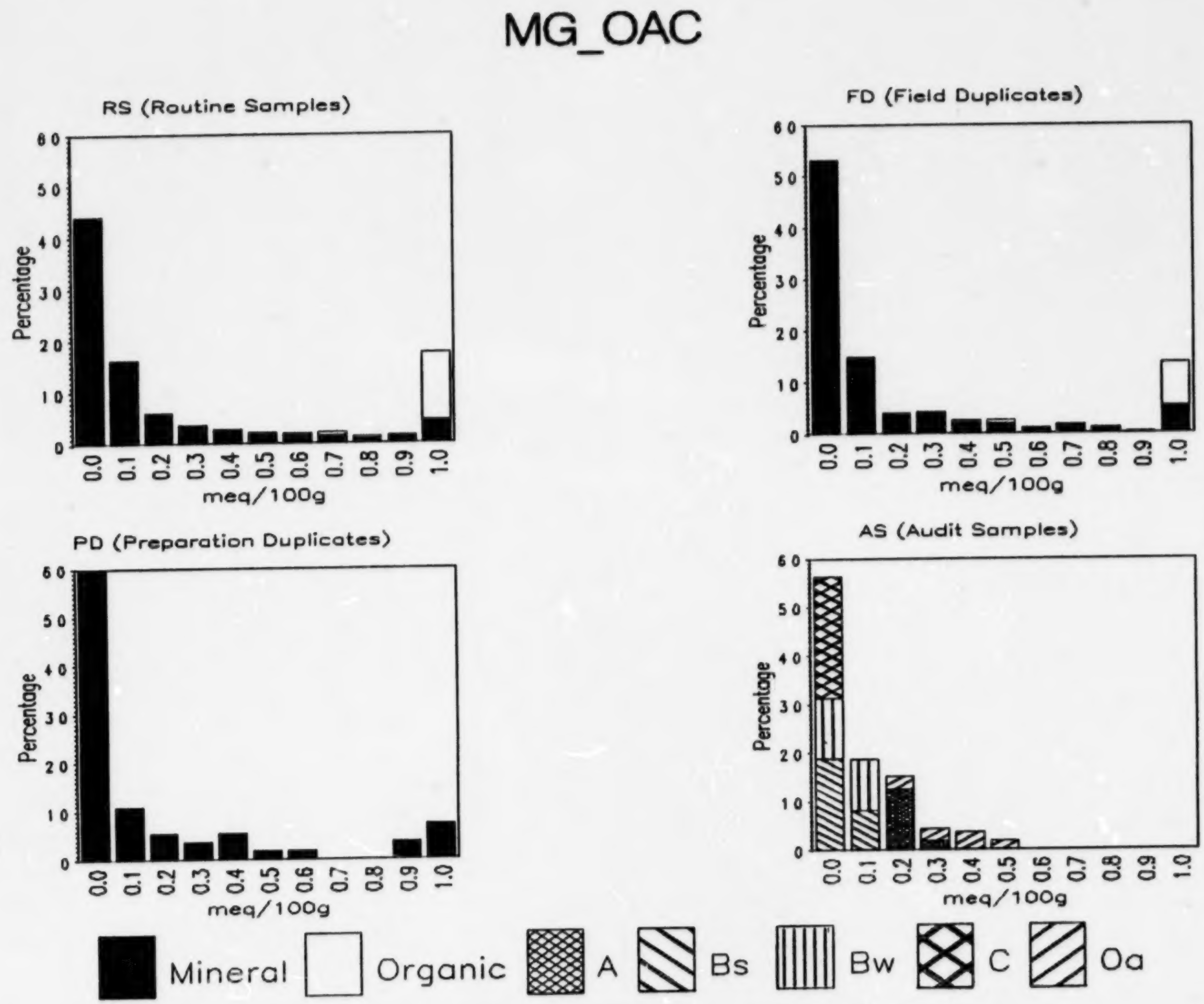


Figure G-21. Range and frequency distribution for magnesium in ammonium acetate.

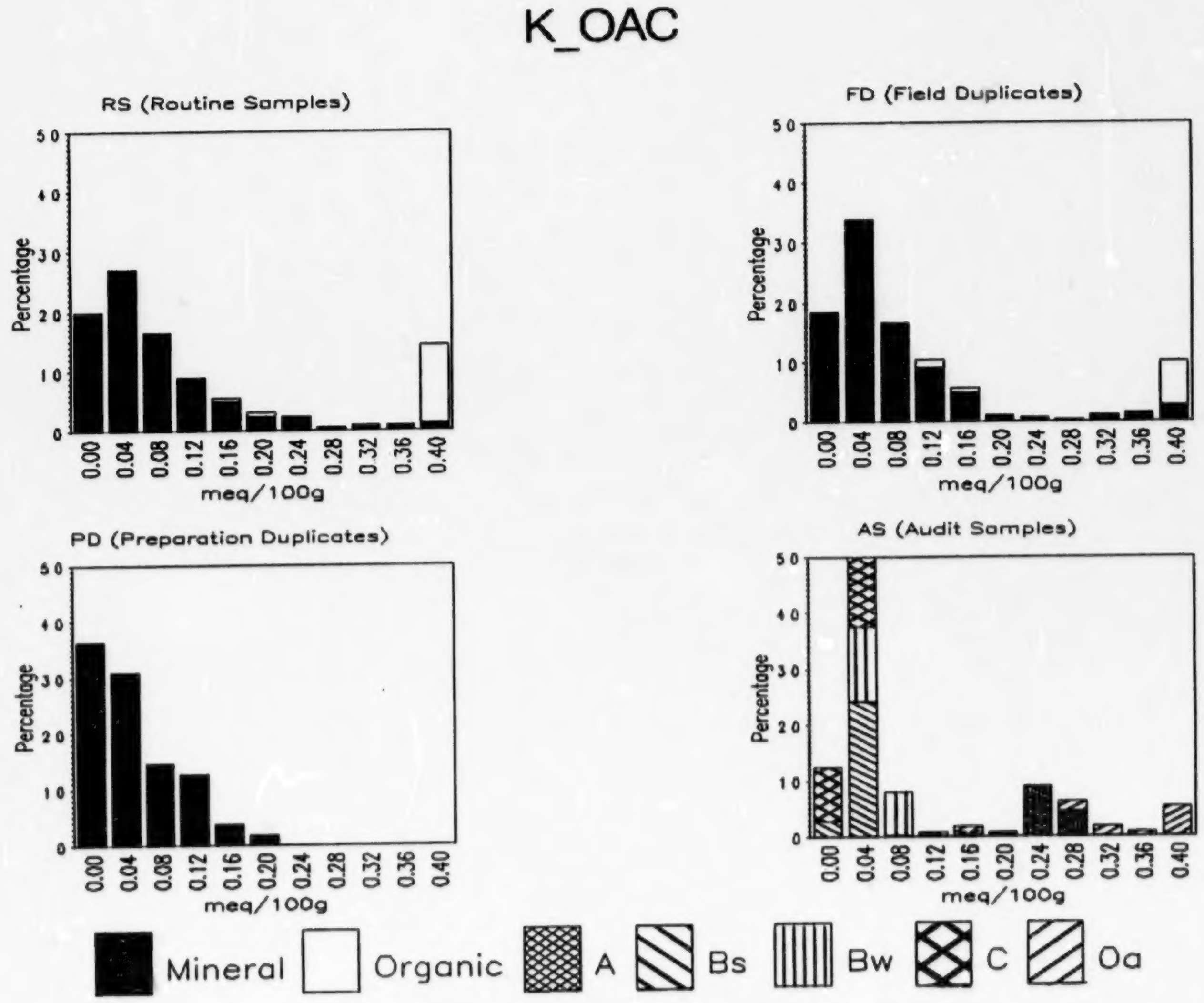


Figure G-22. Range and frequency distribution for potassium in ammonium acetate.

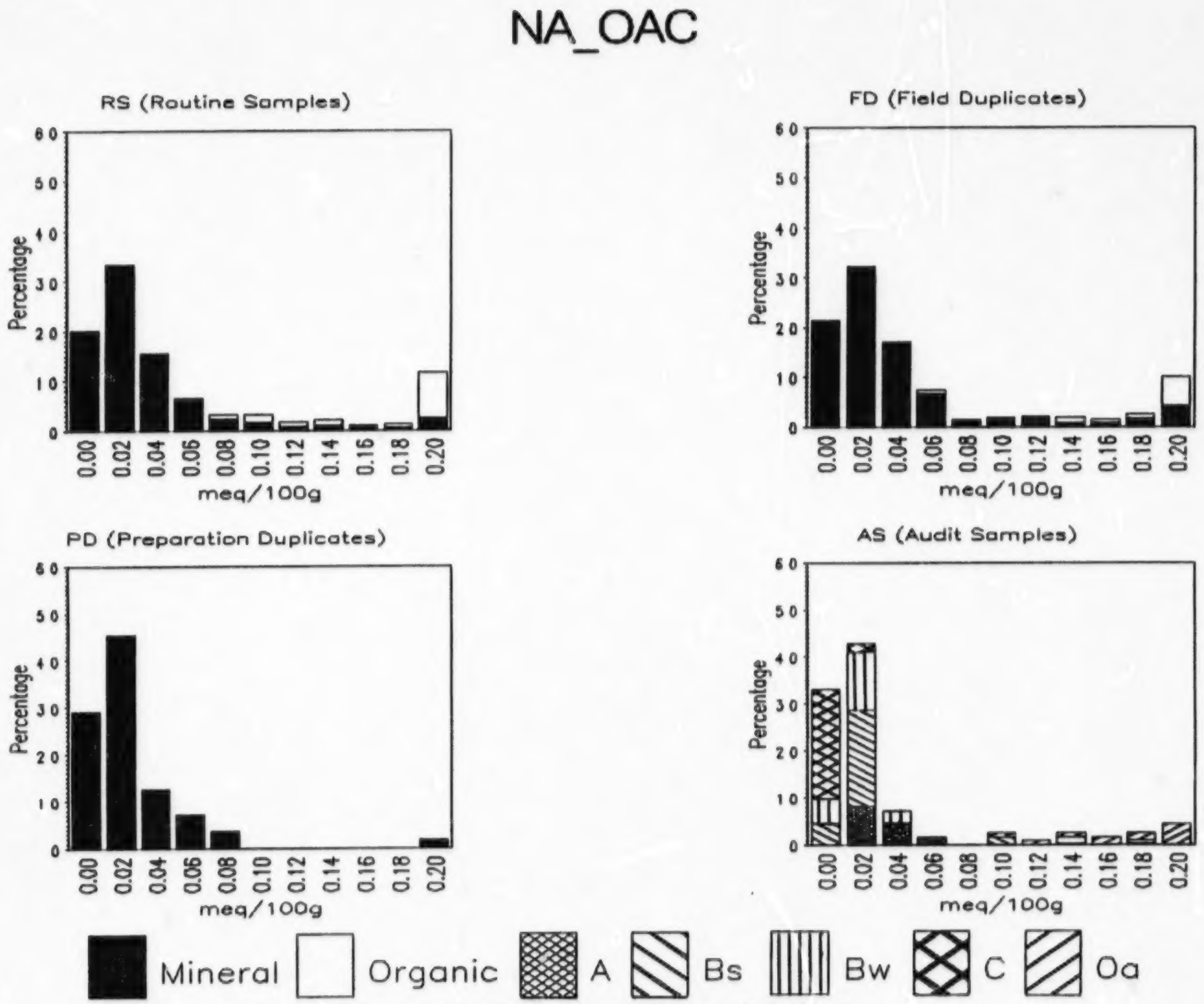


Figure G-23. Range and frequency distribution for sodium in ammonium acetate.

CEC_CL

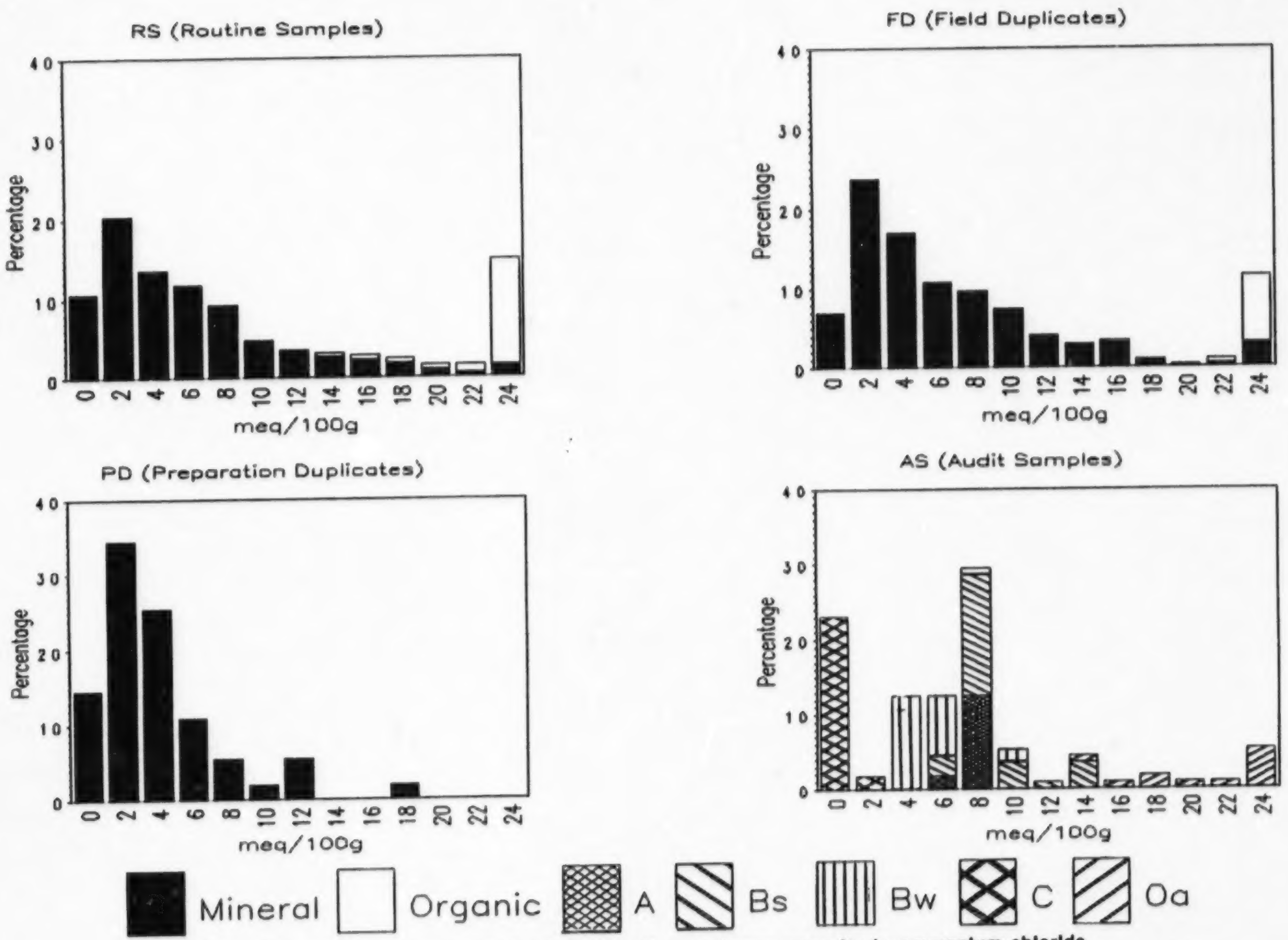


Figure G-24. Range and frequency distribution for cation exchange capacity in ammonium chloride.

CEC_OAC

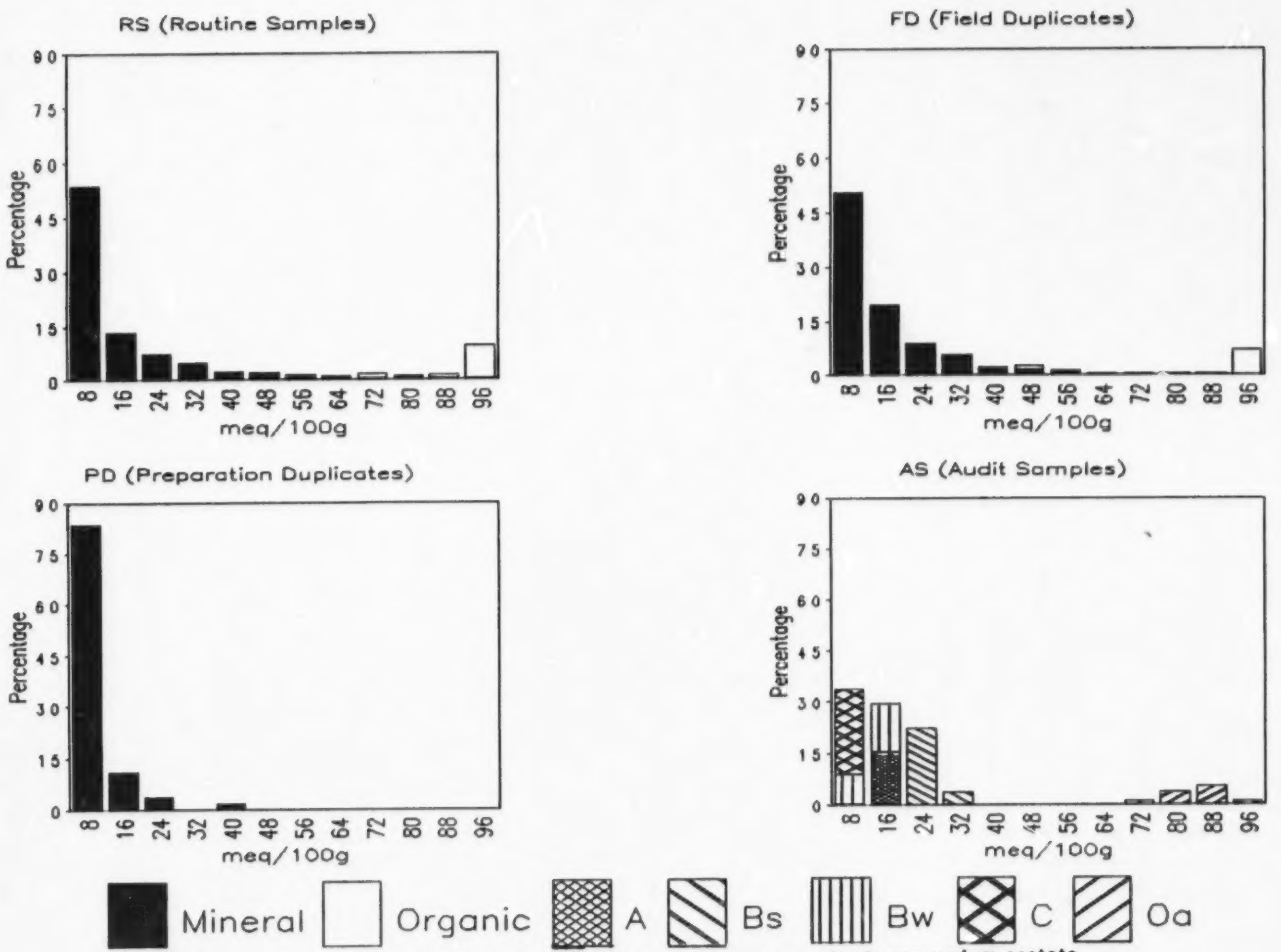


Figure G-25. Range and frequency distribution for cation exchange capacity in ammonium acetate.

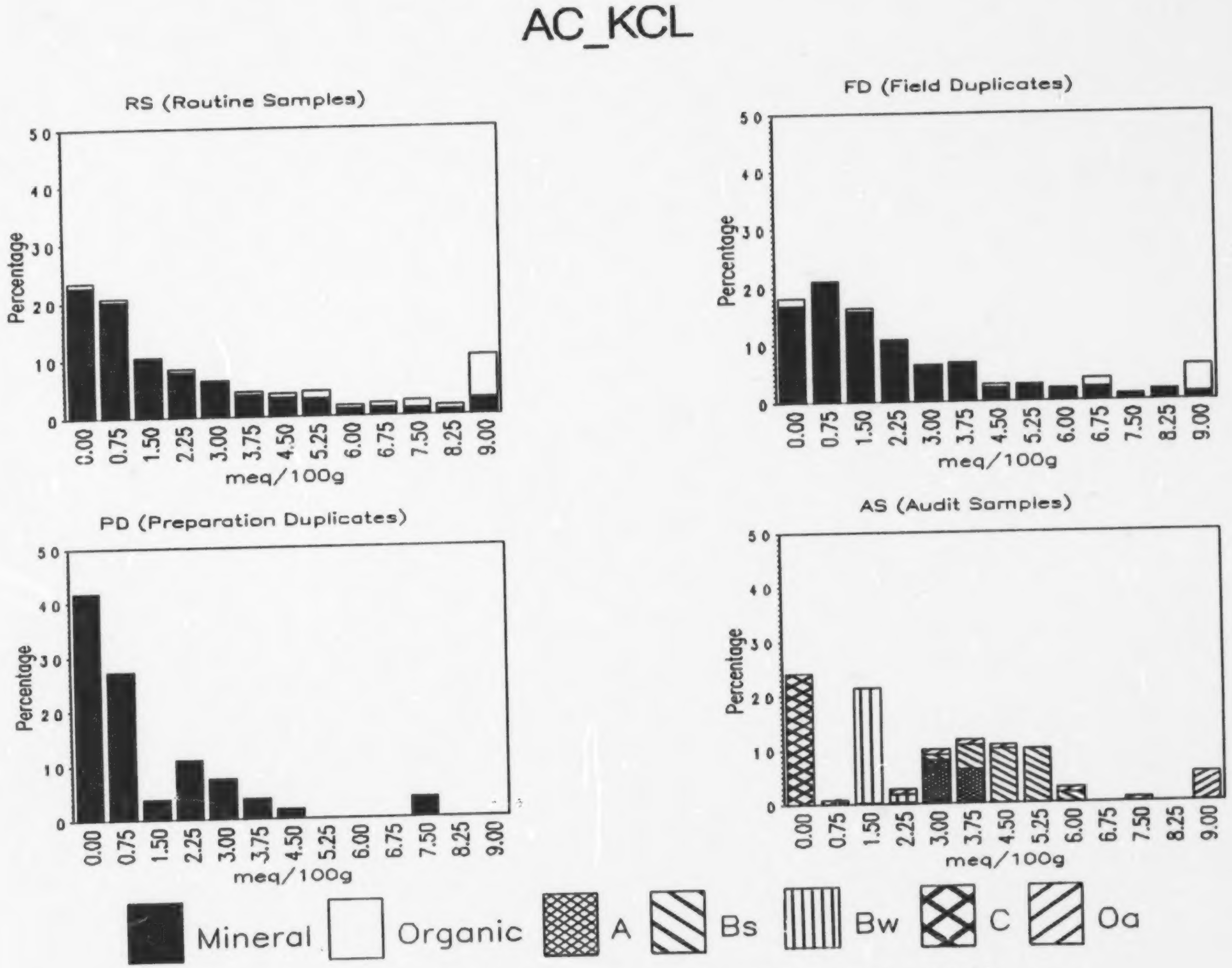


Figure G-26. Range and frequency distribution for exchangeable acidity in potassium chloride.

AC_BACL

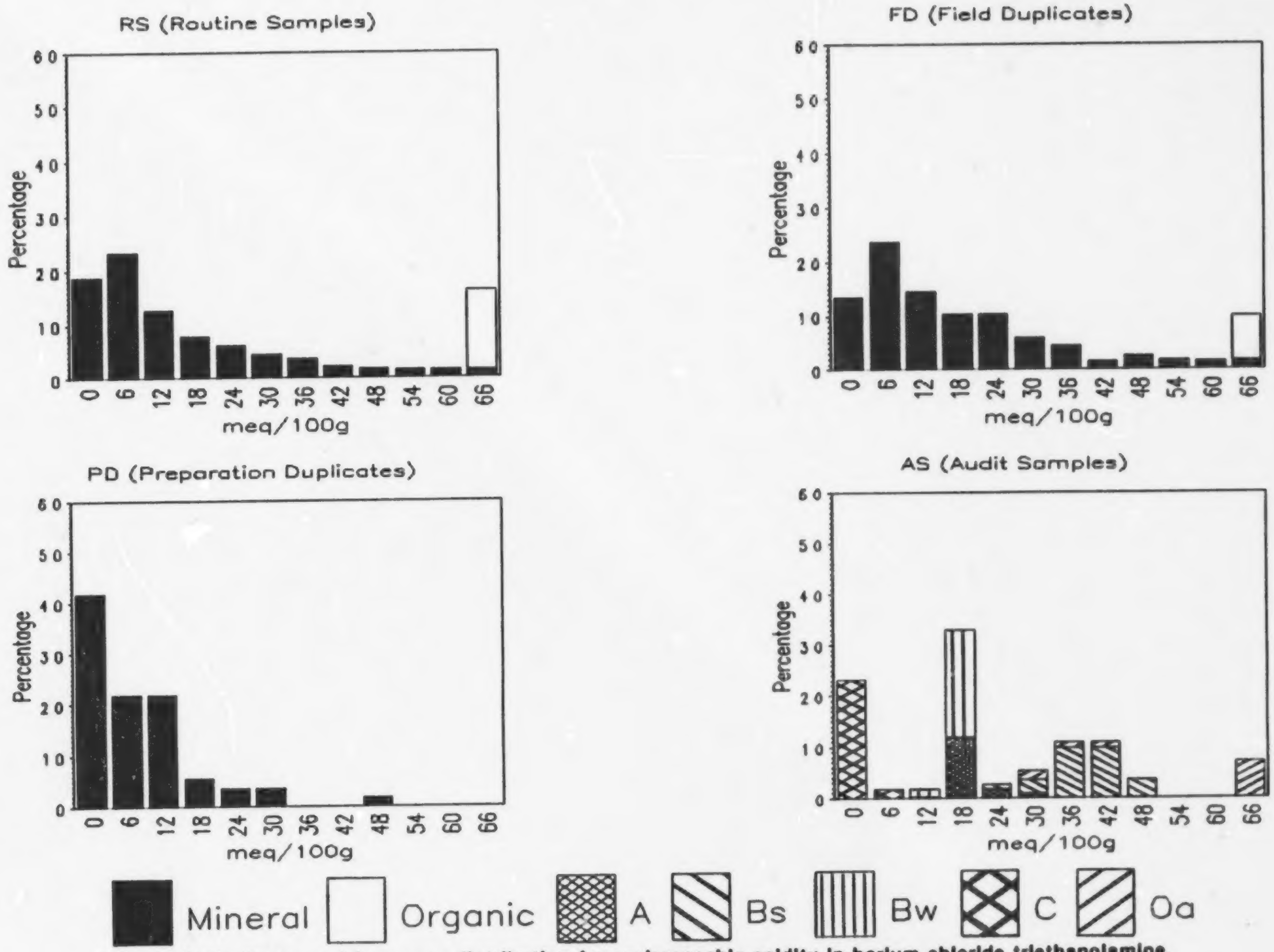


Figure G-27. Range and frequency distribution for exchangeable acidity in barium chloride triethanolamine.

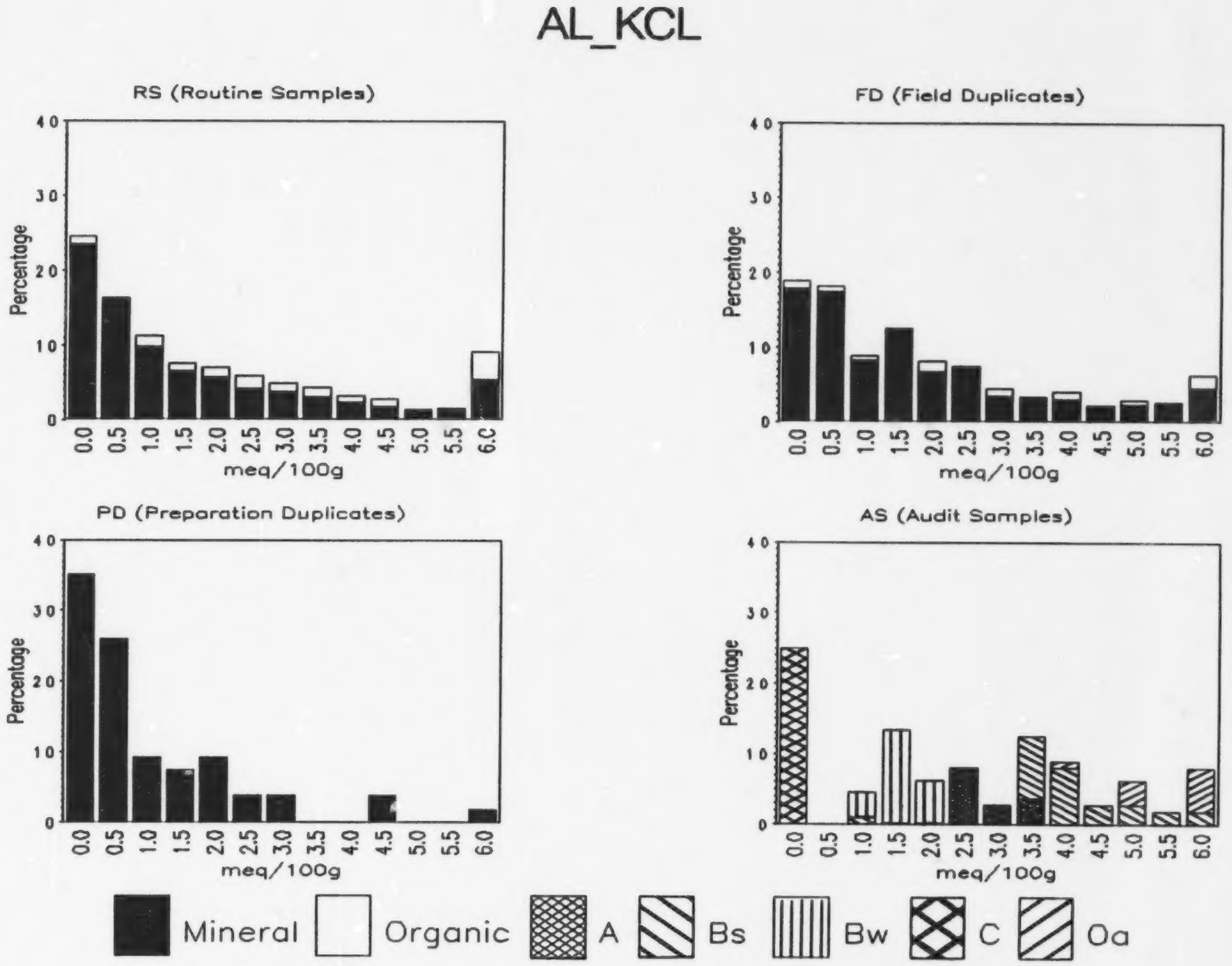


Figure G-28. Range and frequency distribution for exchangeable aluminum in potassium chloride.

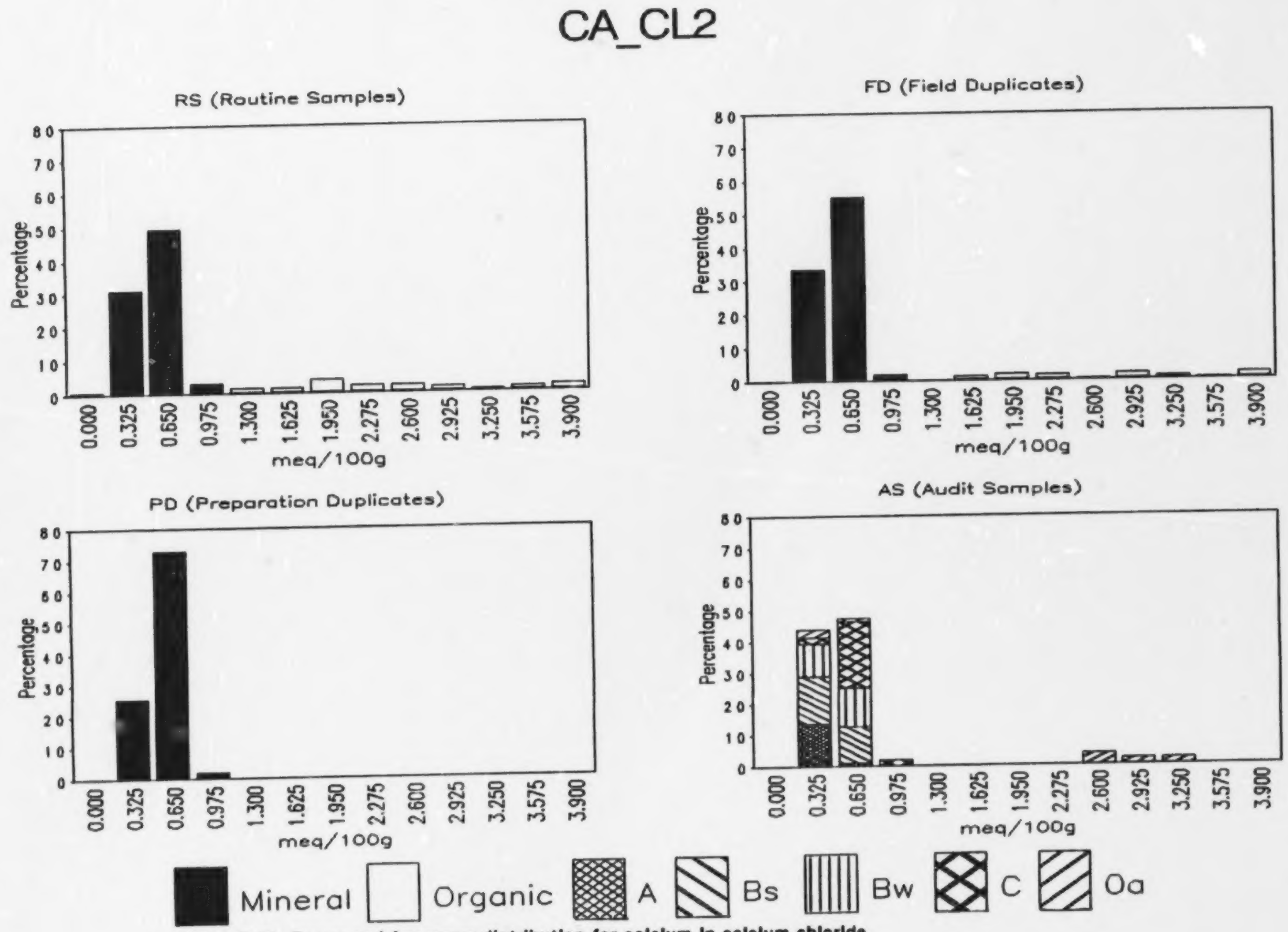


Figure G-29. Range and frequency distribution for calcium in calcium chloride.

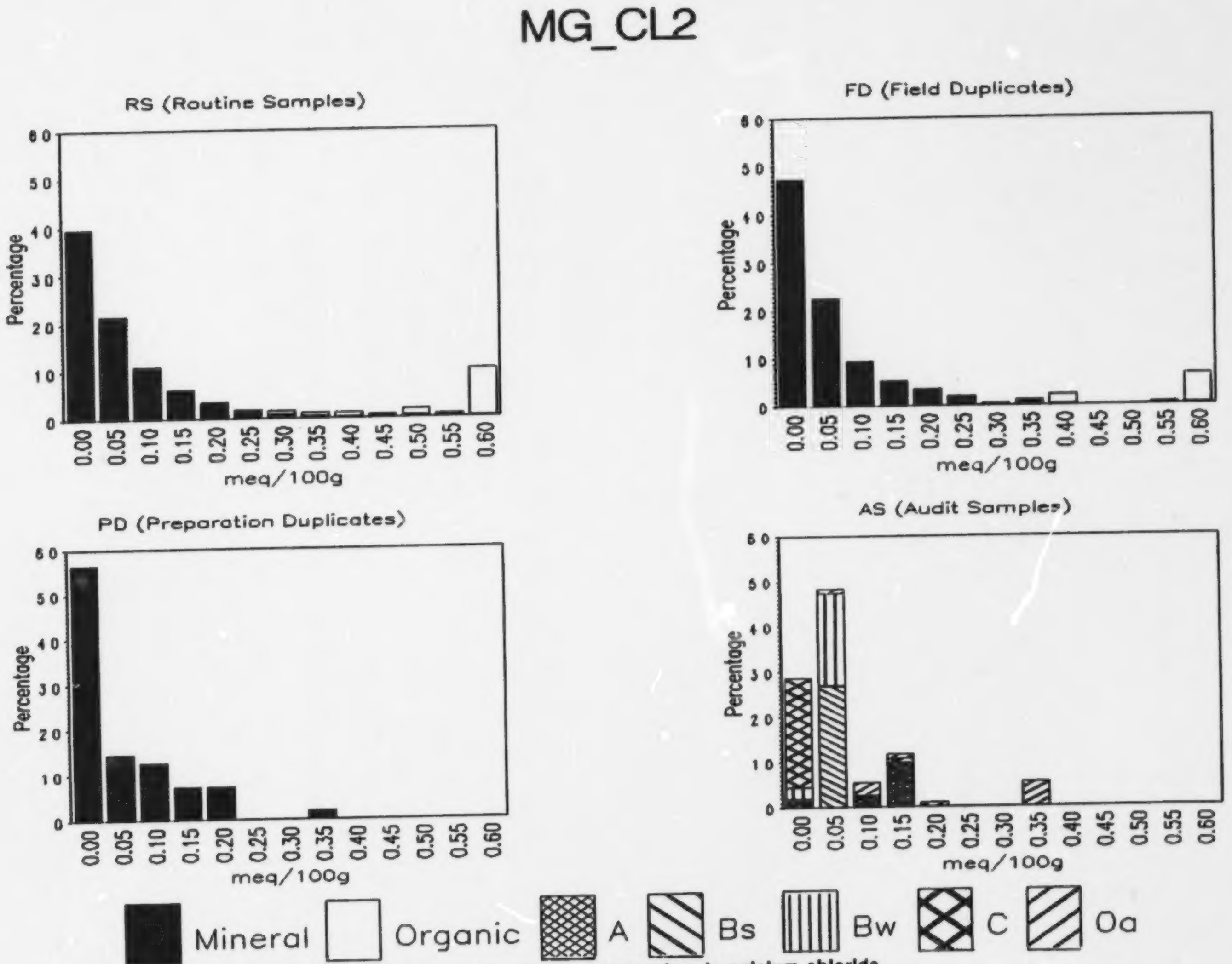


Figure G-30. Range and frequency distribution for magnesium in calcium chloride.

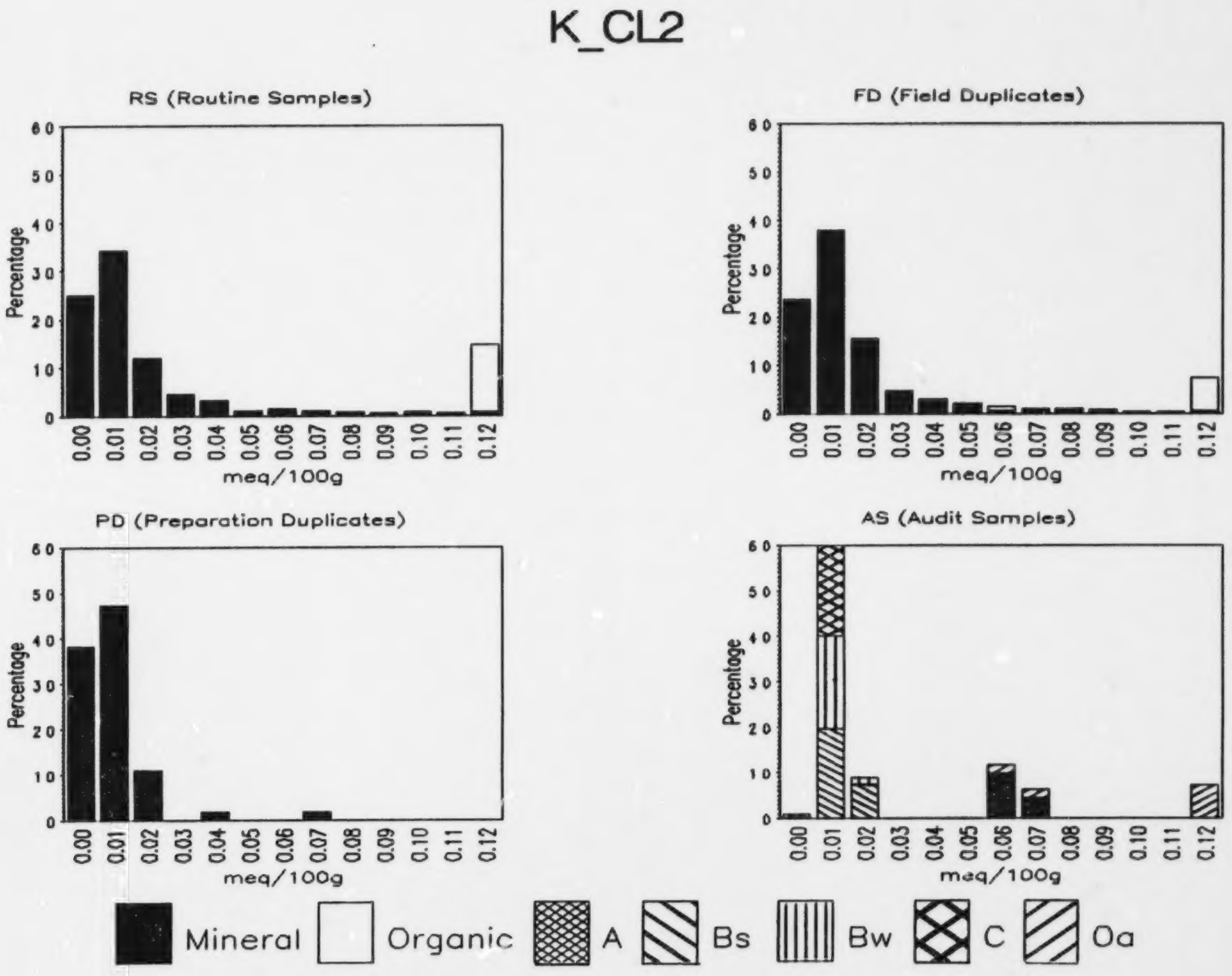


Figure G-31. Range and frequency distribution for potassium in calcium chloride.

NA_CL2

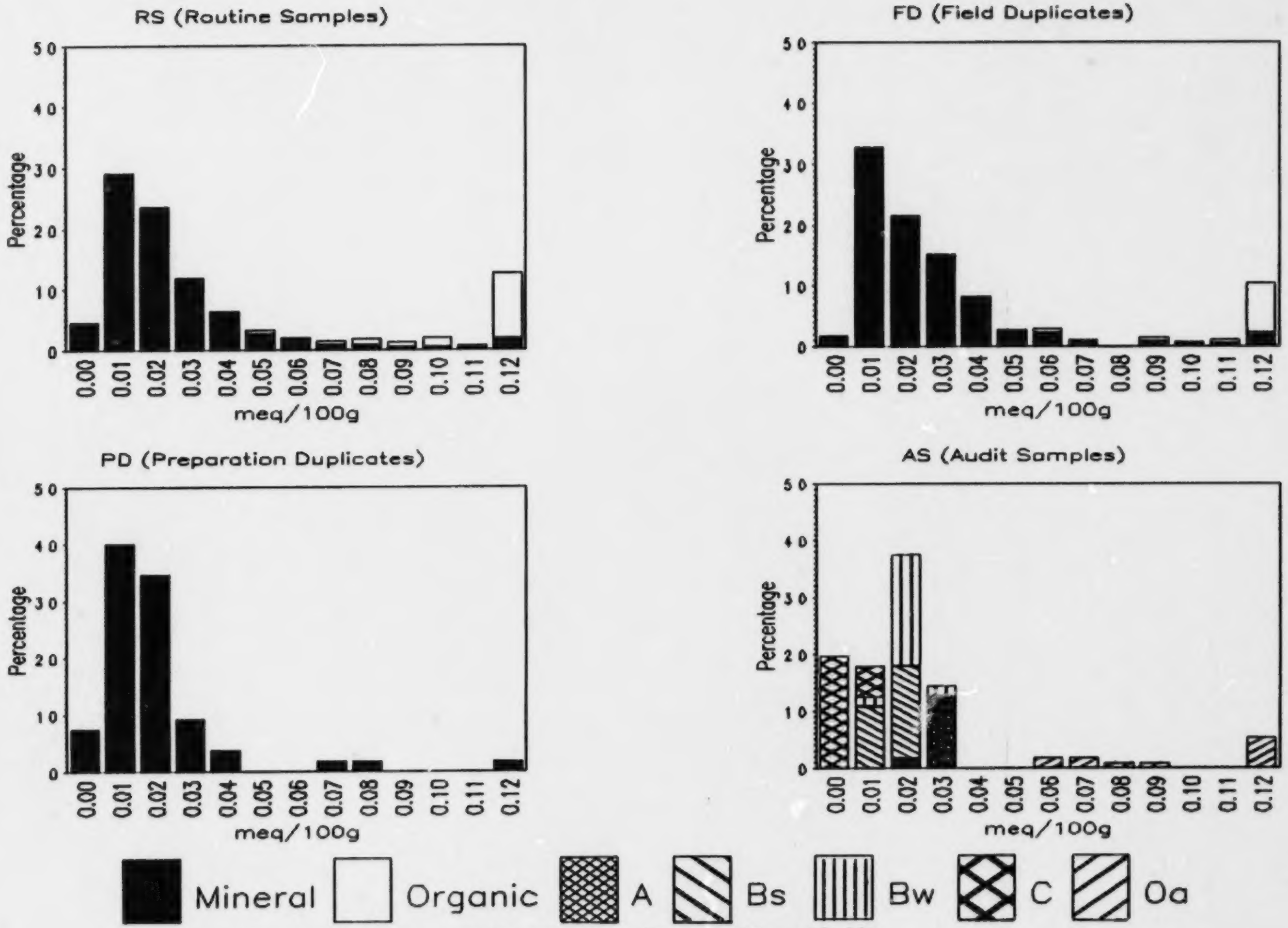


Figure G-32. Range and frequency distribution for sodium in calcium chloride.

FE_CL2

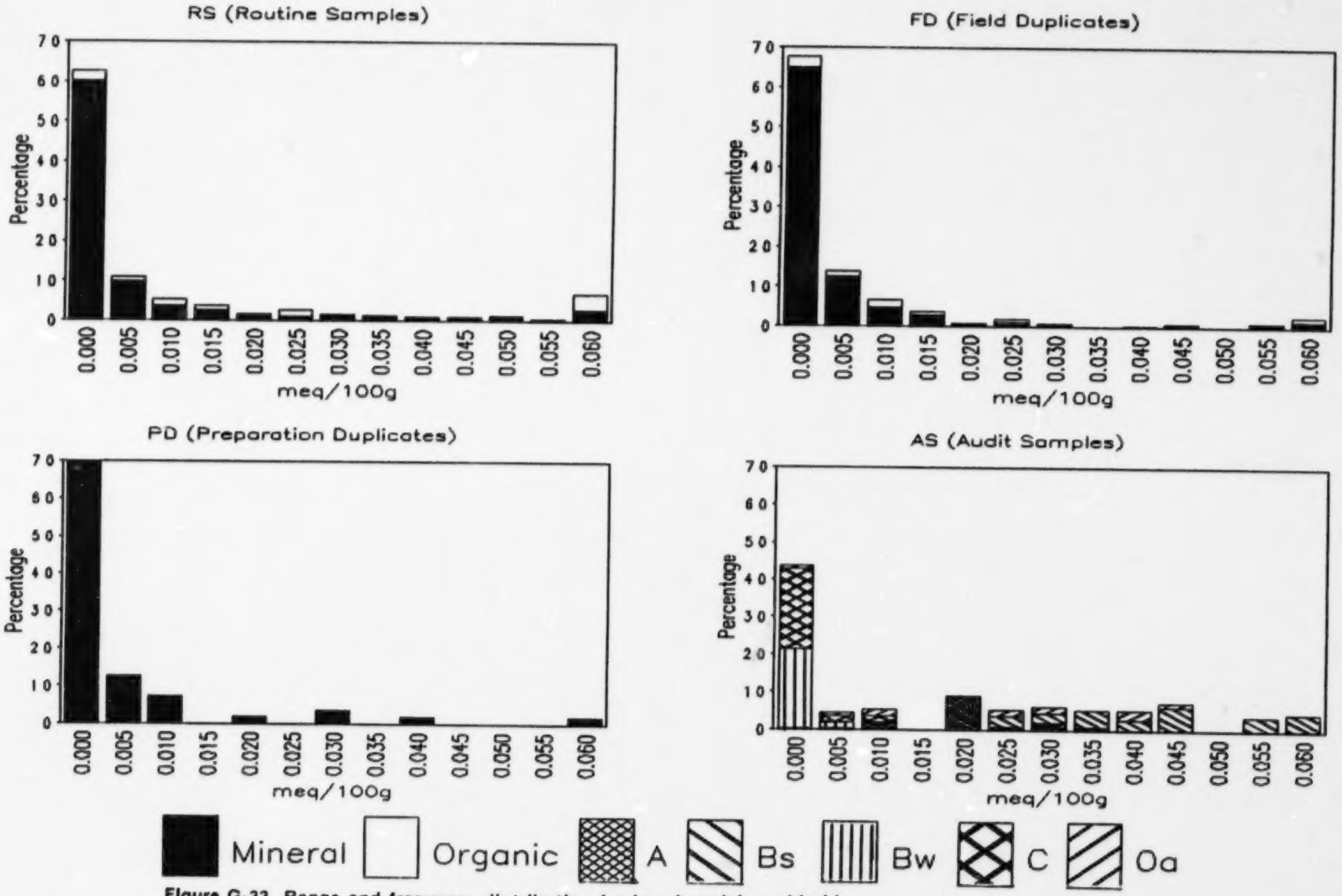


Figure G-33. Range and frequency distribution for iron in calcium chloride.

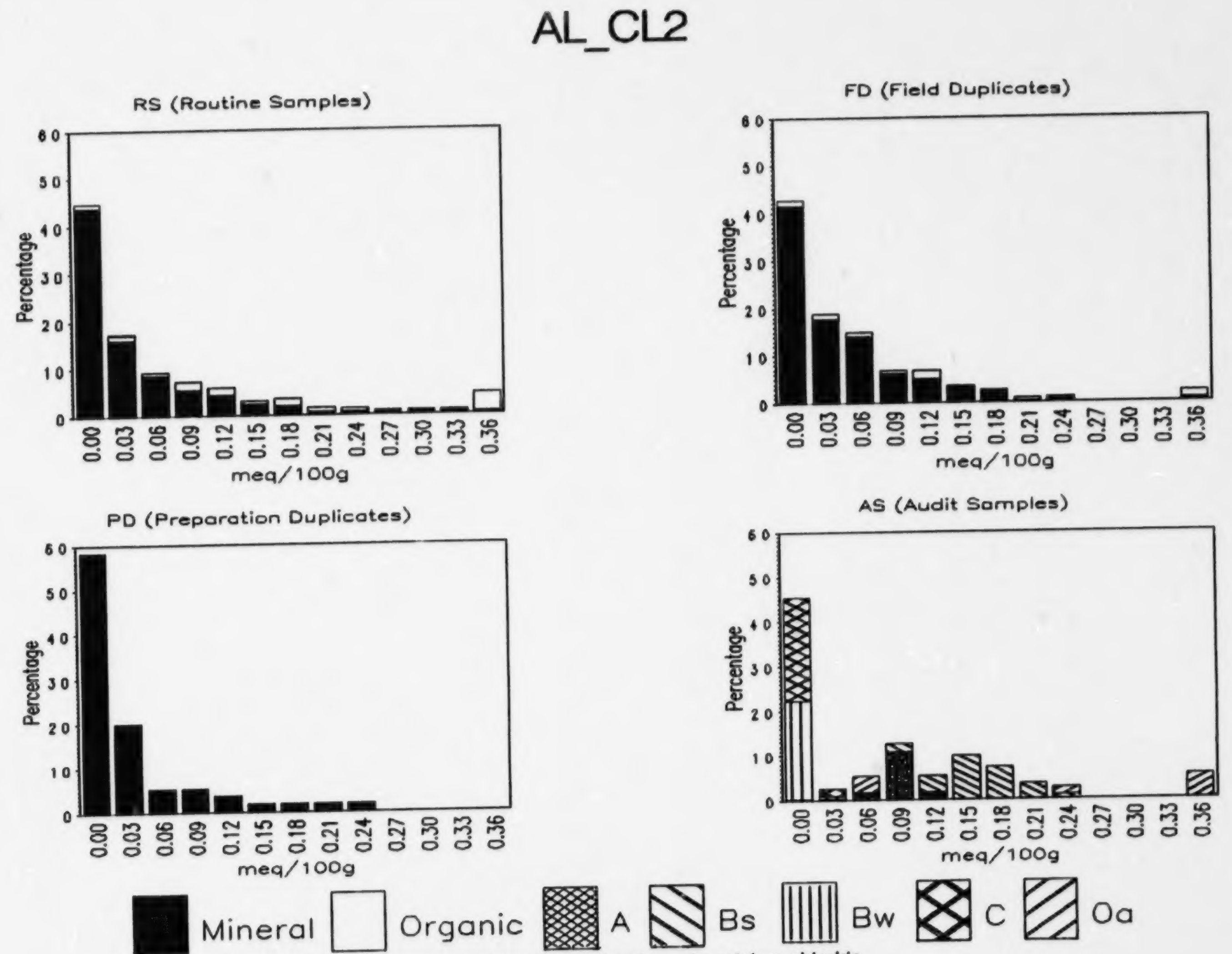


Figure G-34. Range and frequency distribution for aluminum in calcium chloride.

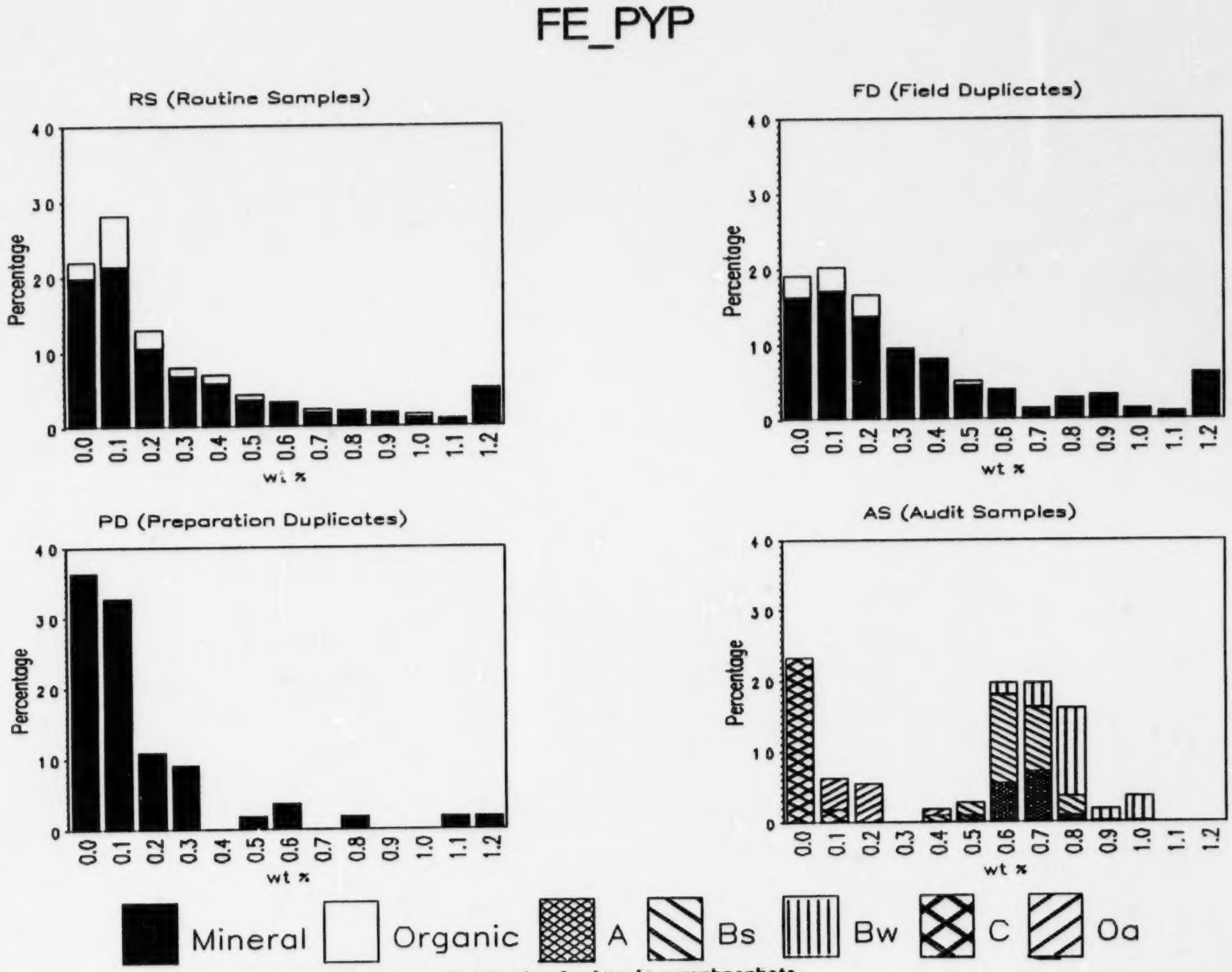


Figure G-35. Range and frequency distribution for iron in pyrophosphate.

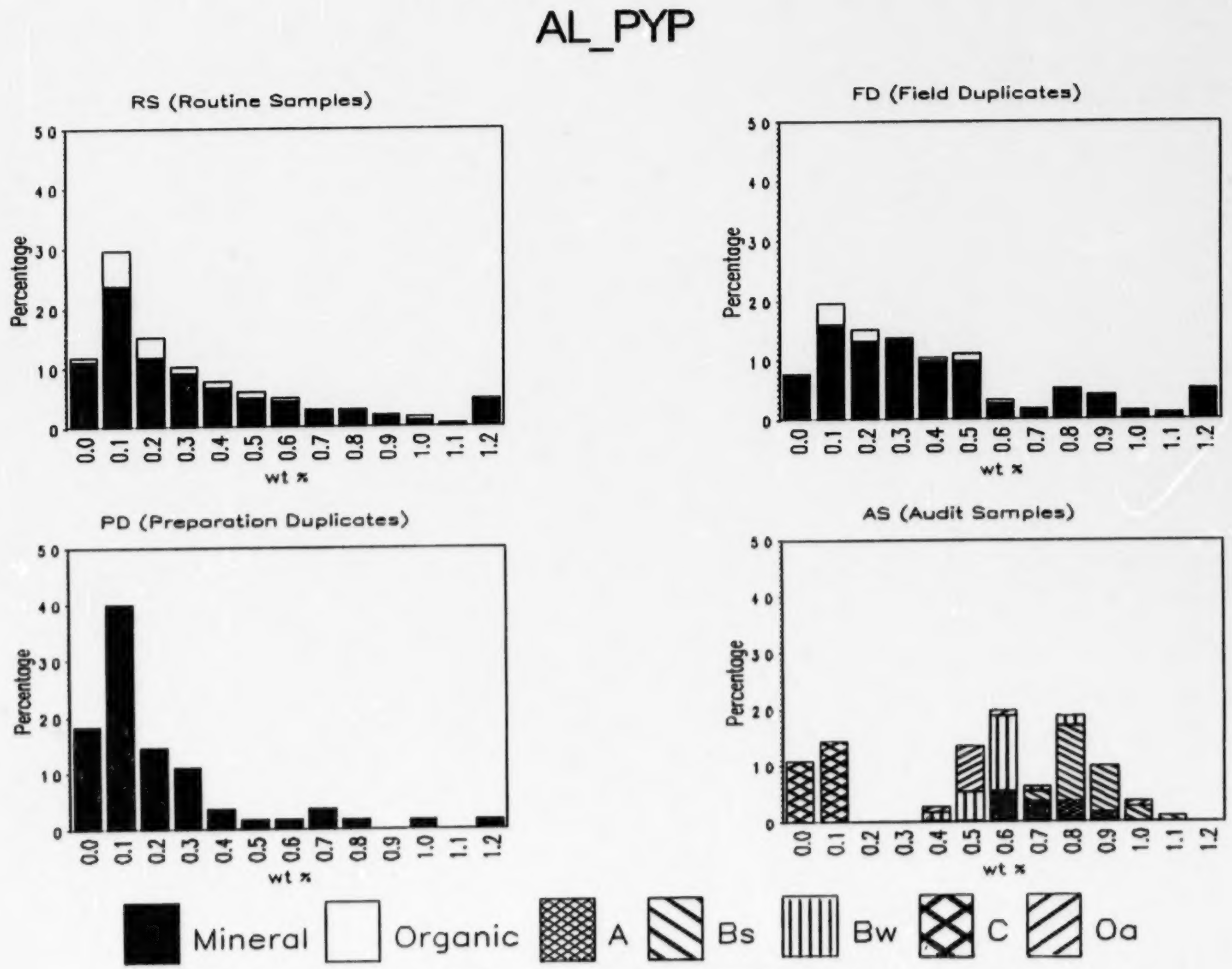


Figure G-36. Range and frequency distribution for aluminum in pyrophosphate.

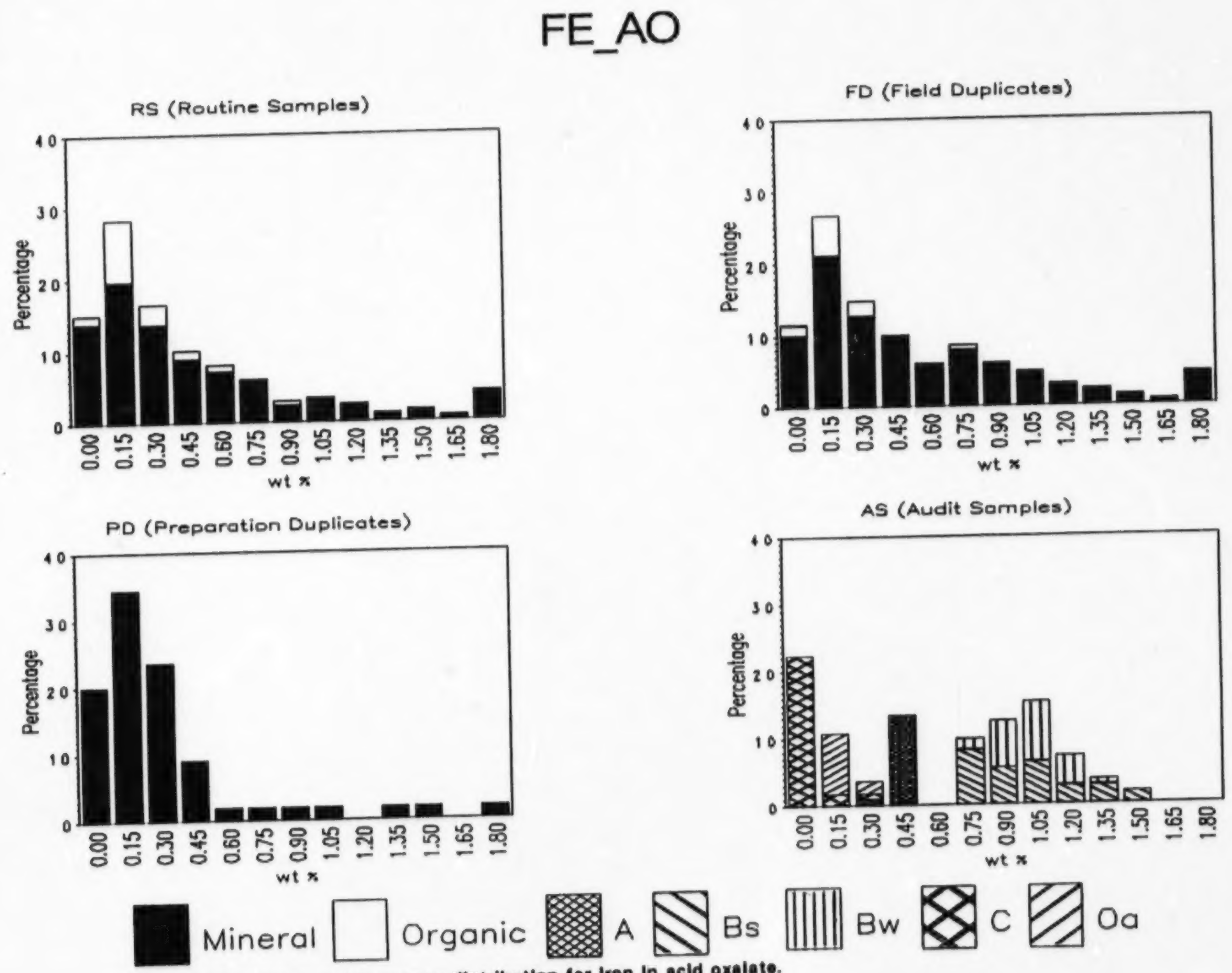


Figure G-37. Range and frequency distribution for iron in acid oxalate.

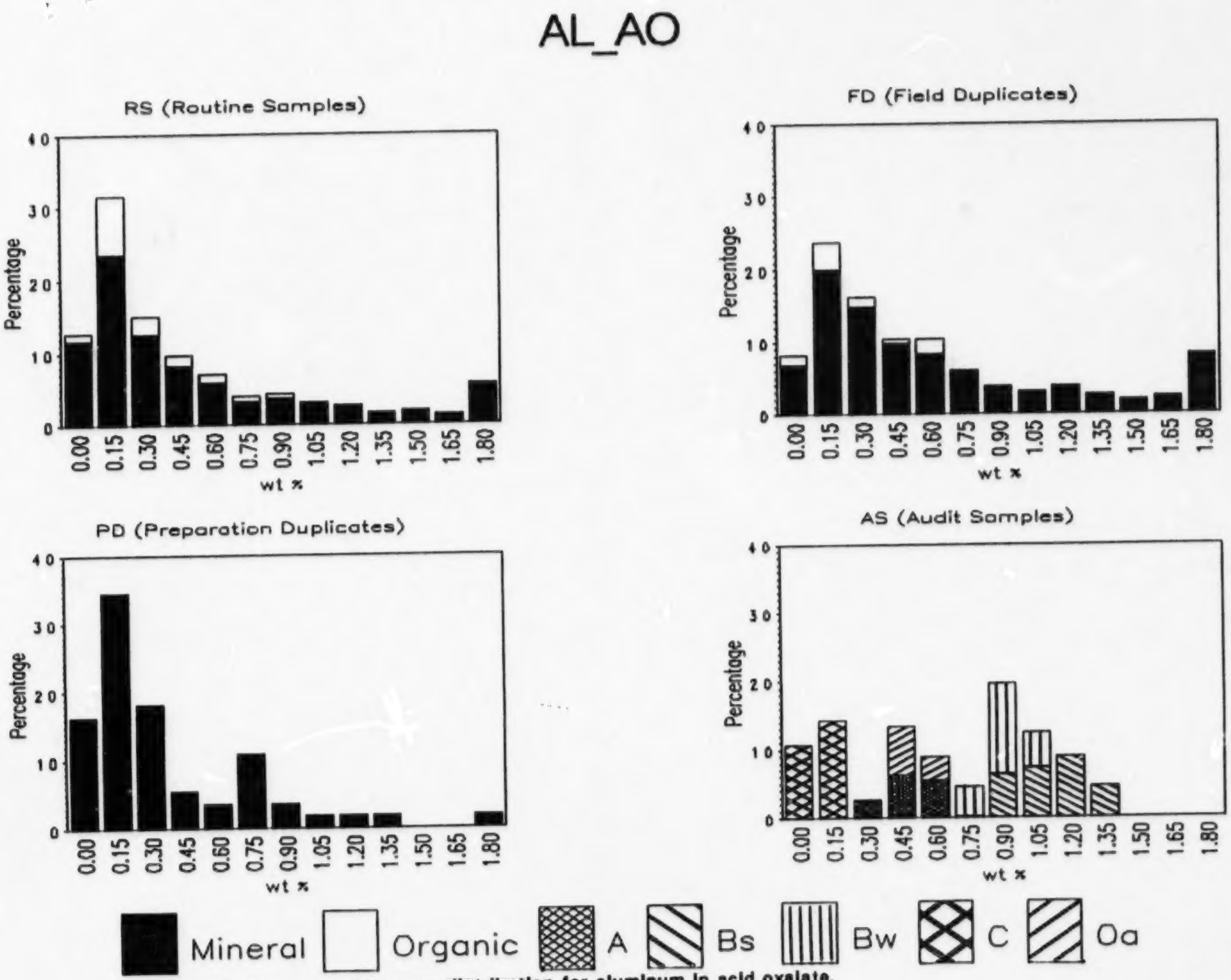


Figure G-38. Range and frequency distribution for aluminum in acid oxalate.

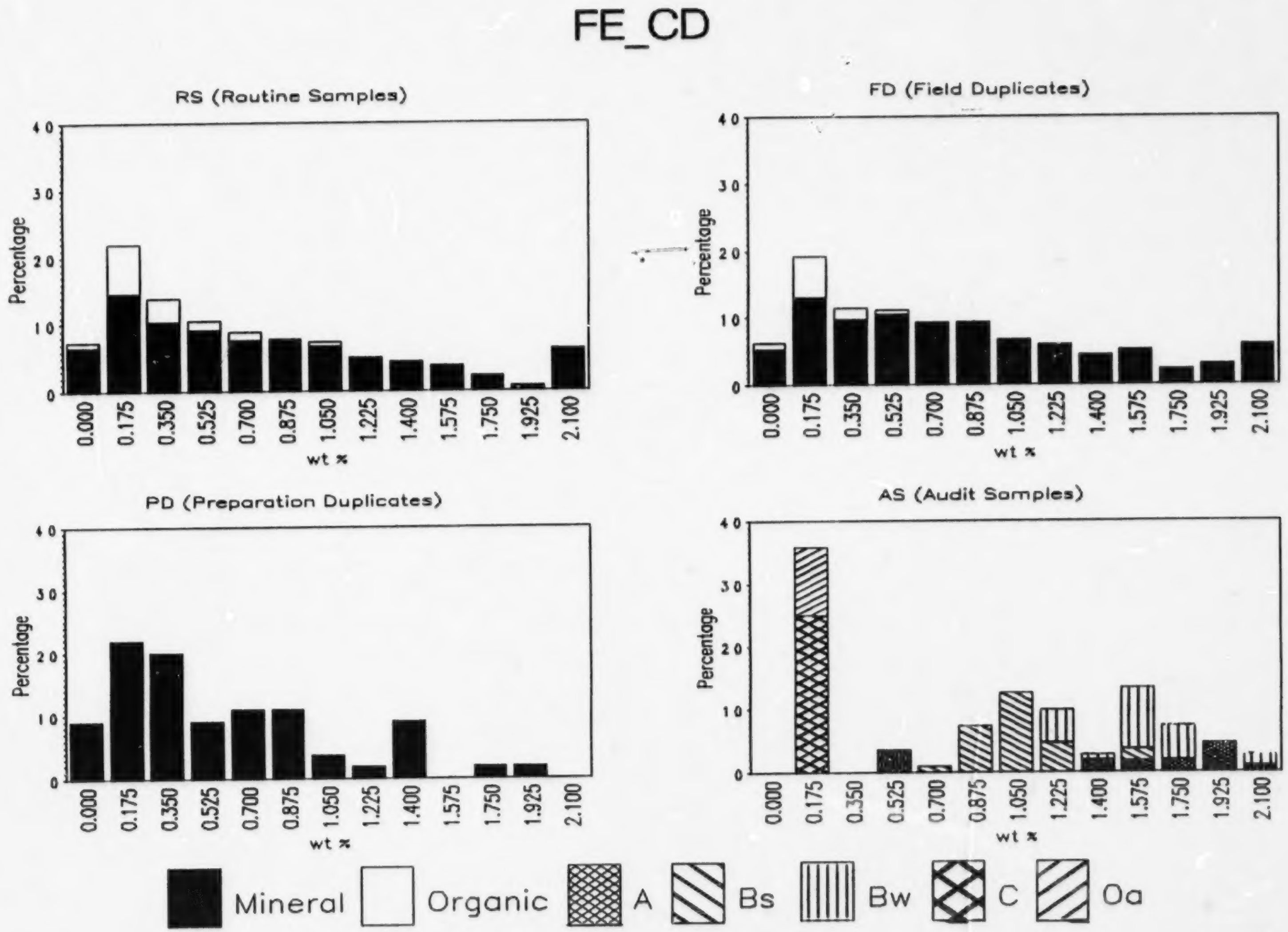


Figure G-39. Range and frequency distribution for iron in citrate dithionite.

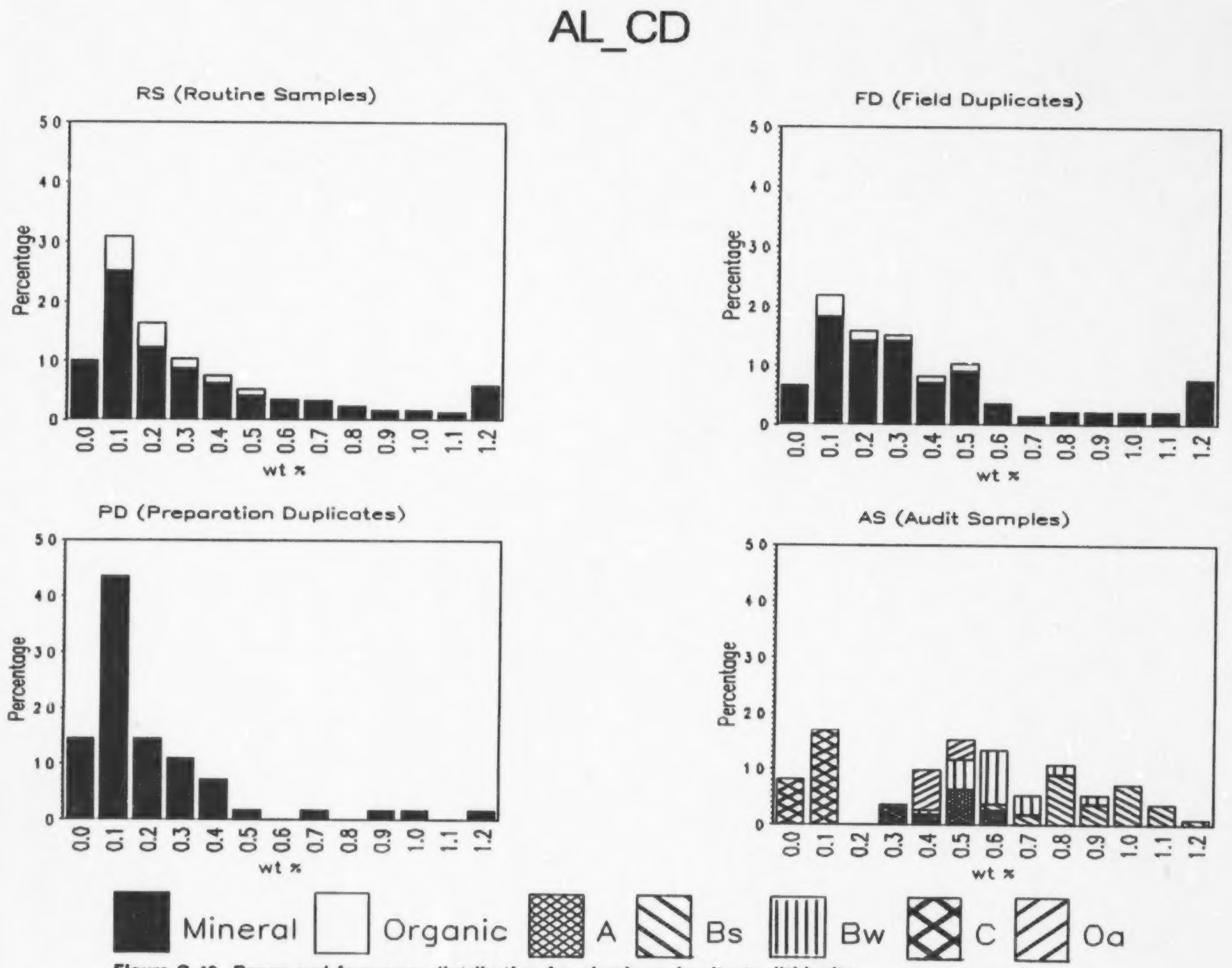


Figure G-40. Range and frequency distribution for aluminum in citrate dithionite.

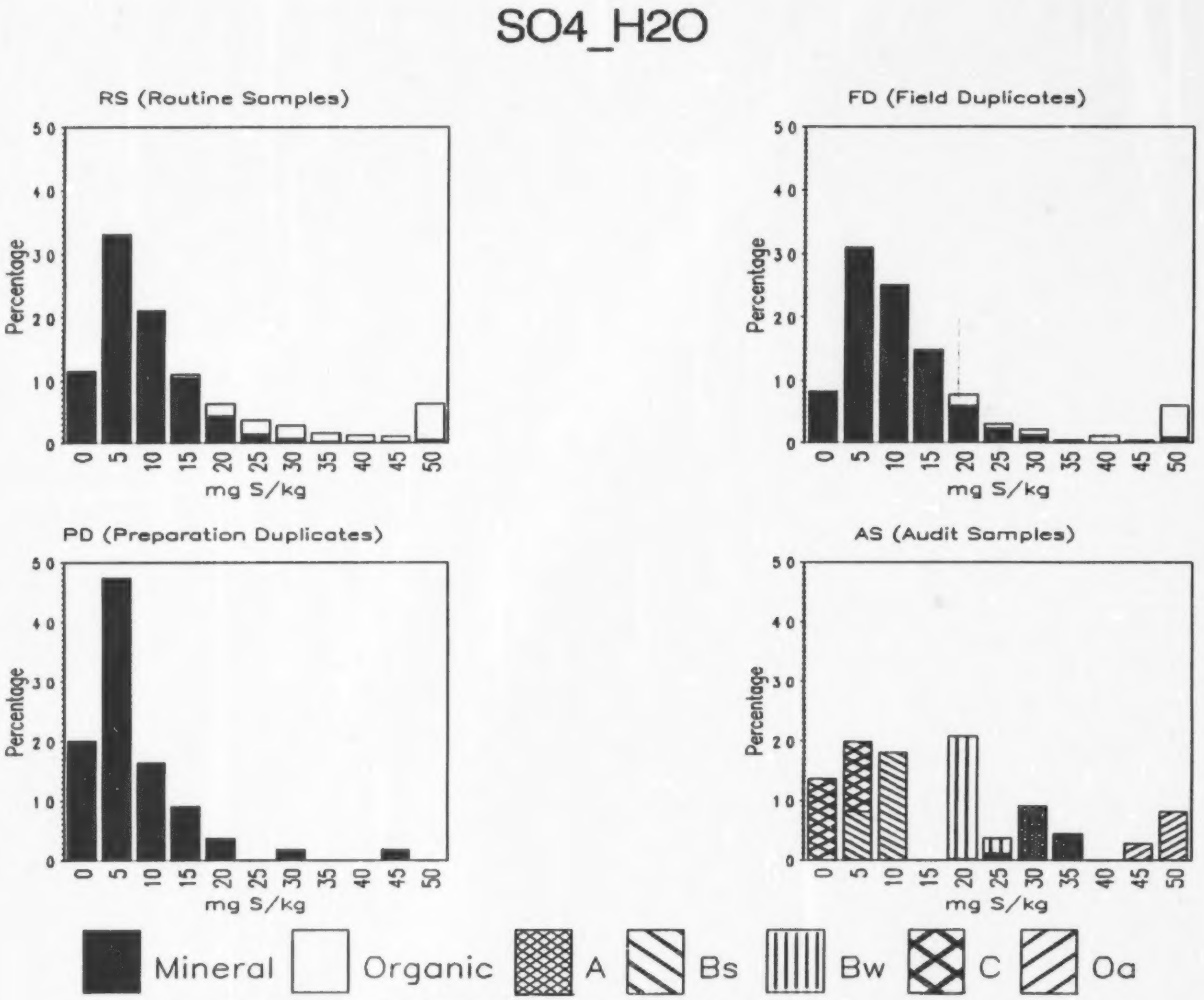


Figure G-41. Range and frequency distribution for water-extractable sulfate.

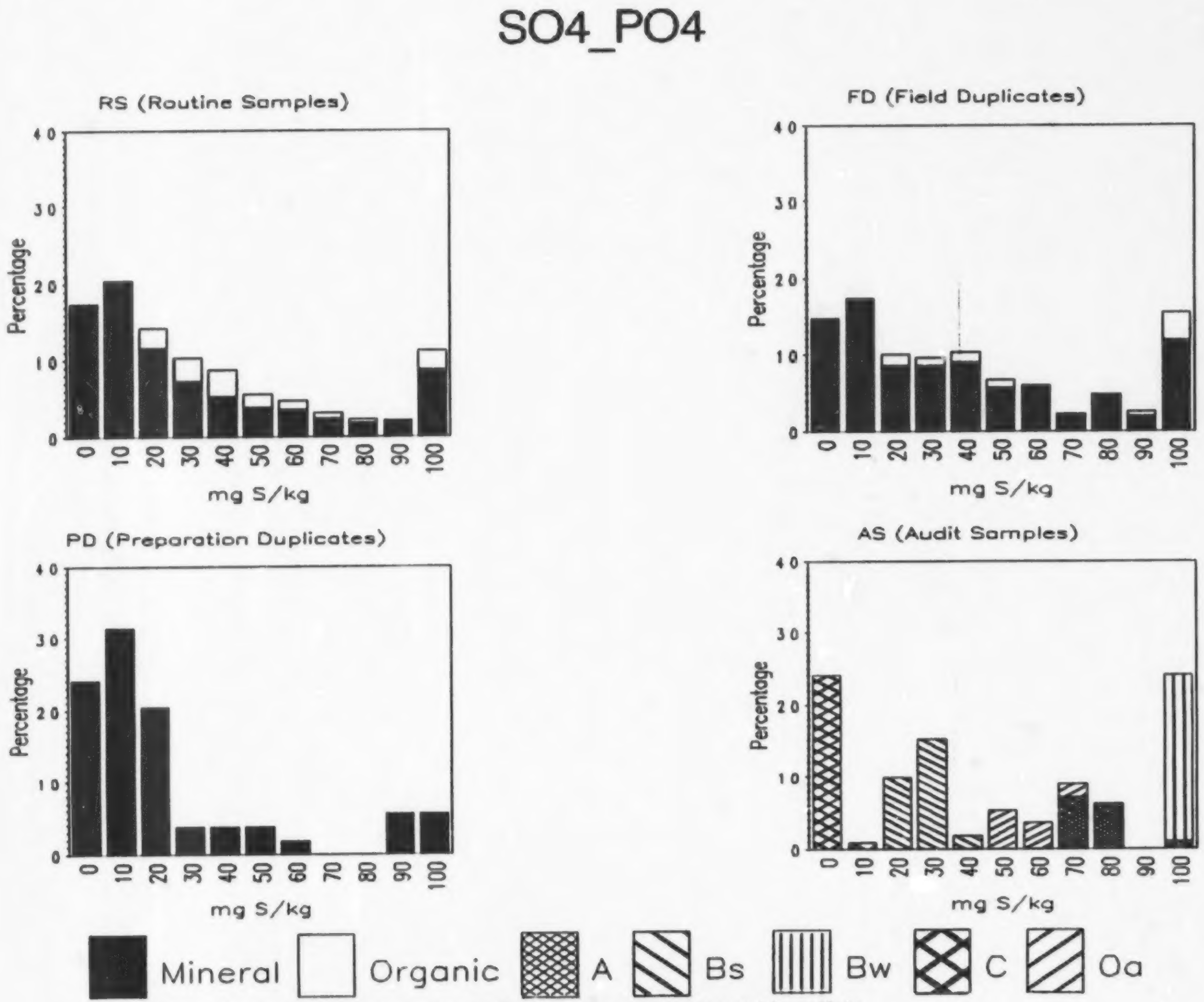


Figure G-42. Range and frequency distribution for phosphate-extractable sulfate.

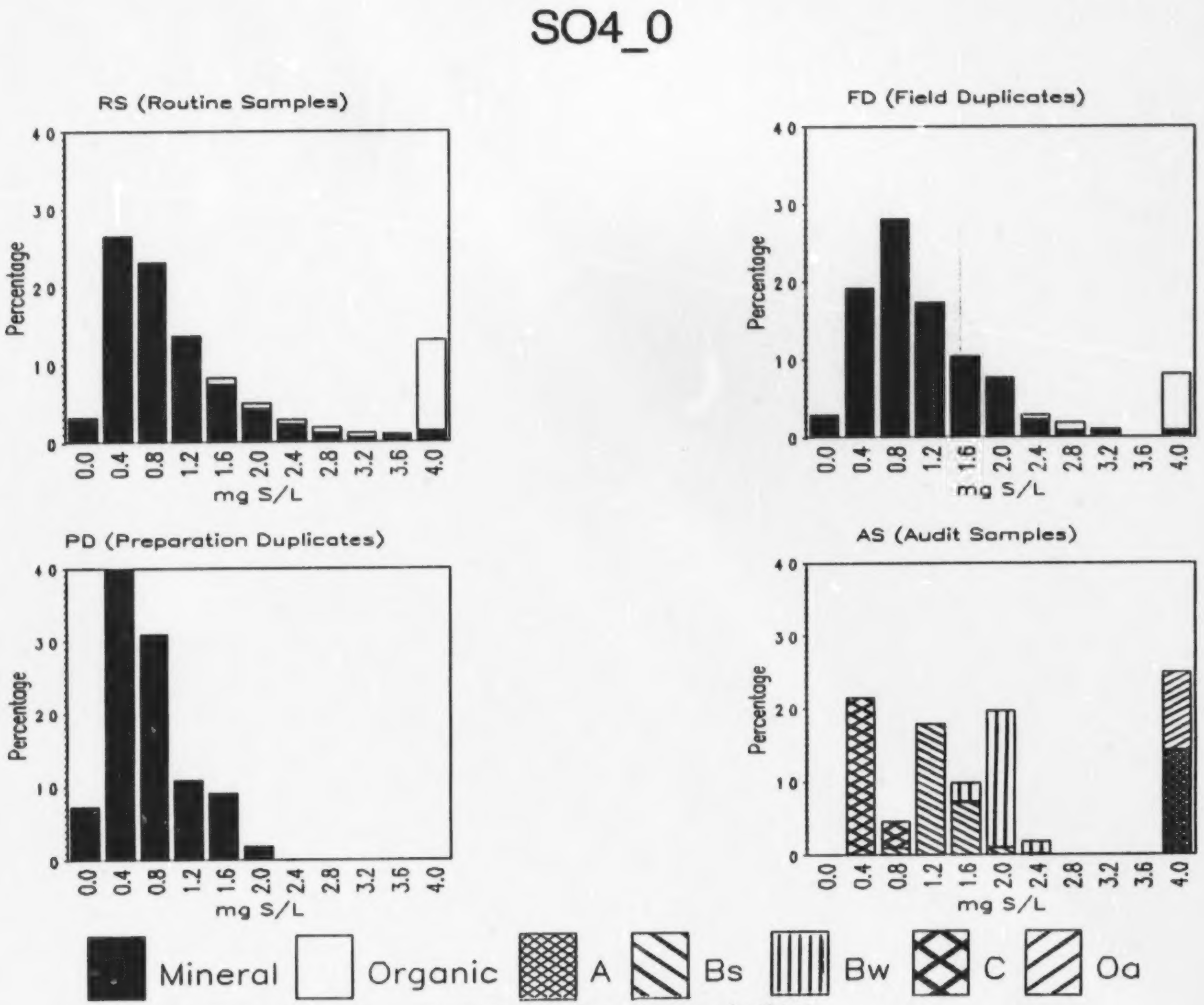


Figure G-43. Range and frequency distribution for the sulfate-zero isotherm.

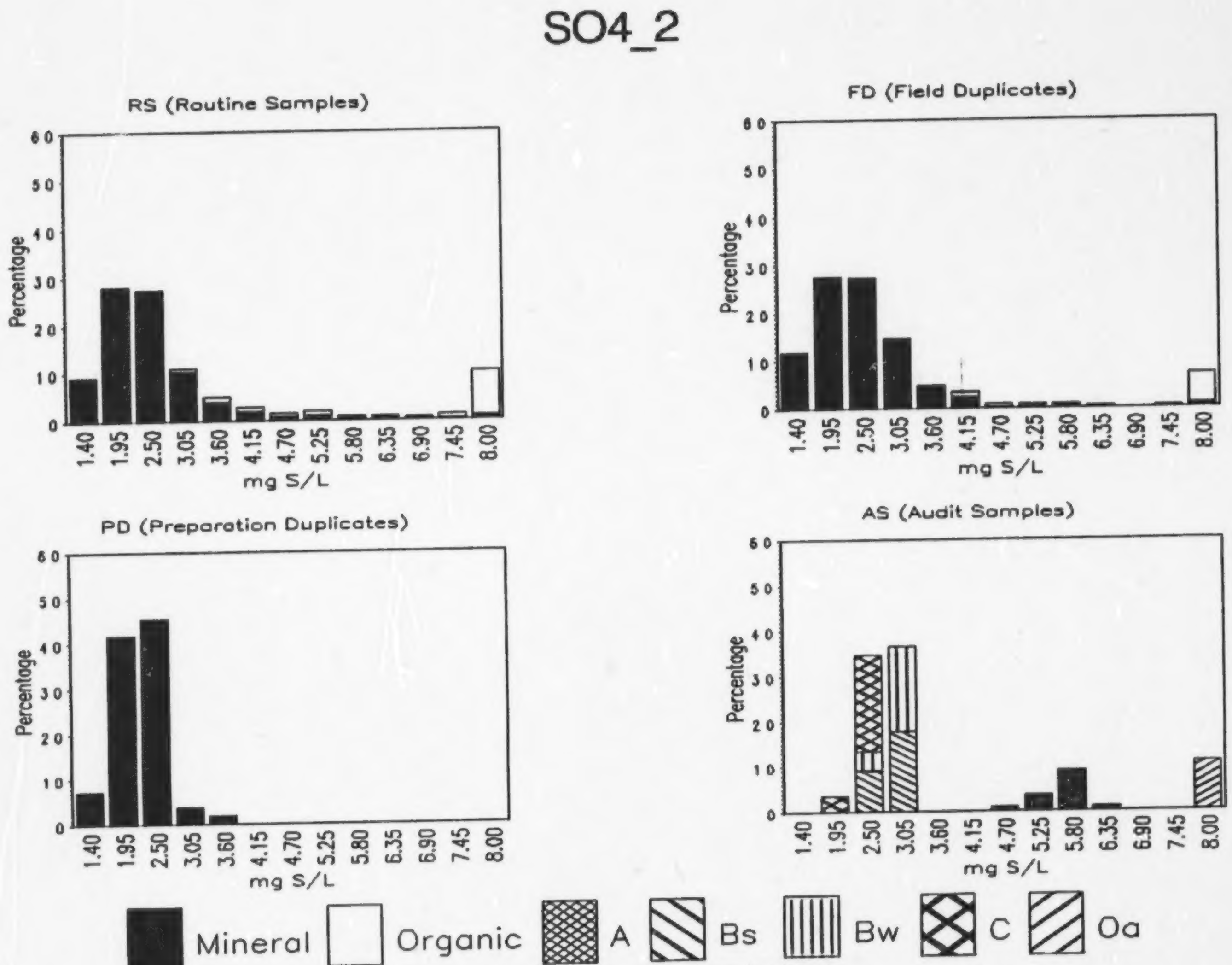


Figure G-44. Range and frequency distribution for the sulfate-two isotherm.

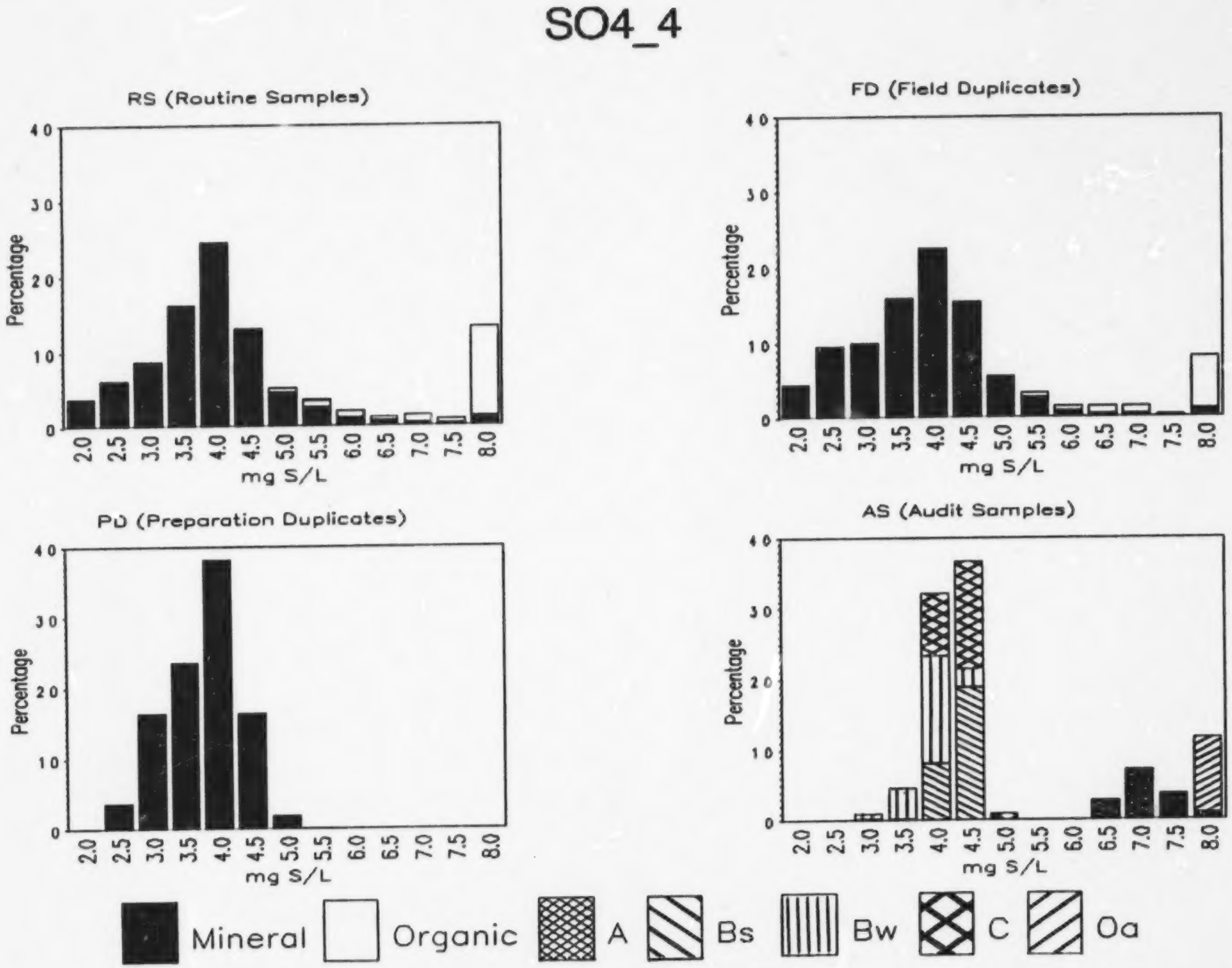


Figure G-45. Range and frequency distribution for the sulfate-four isotherm.

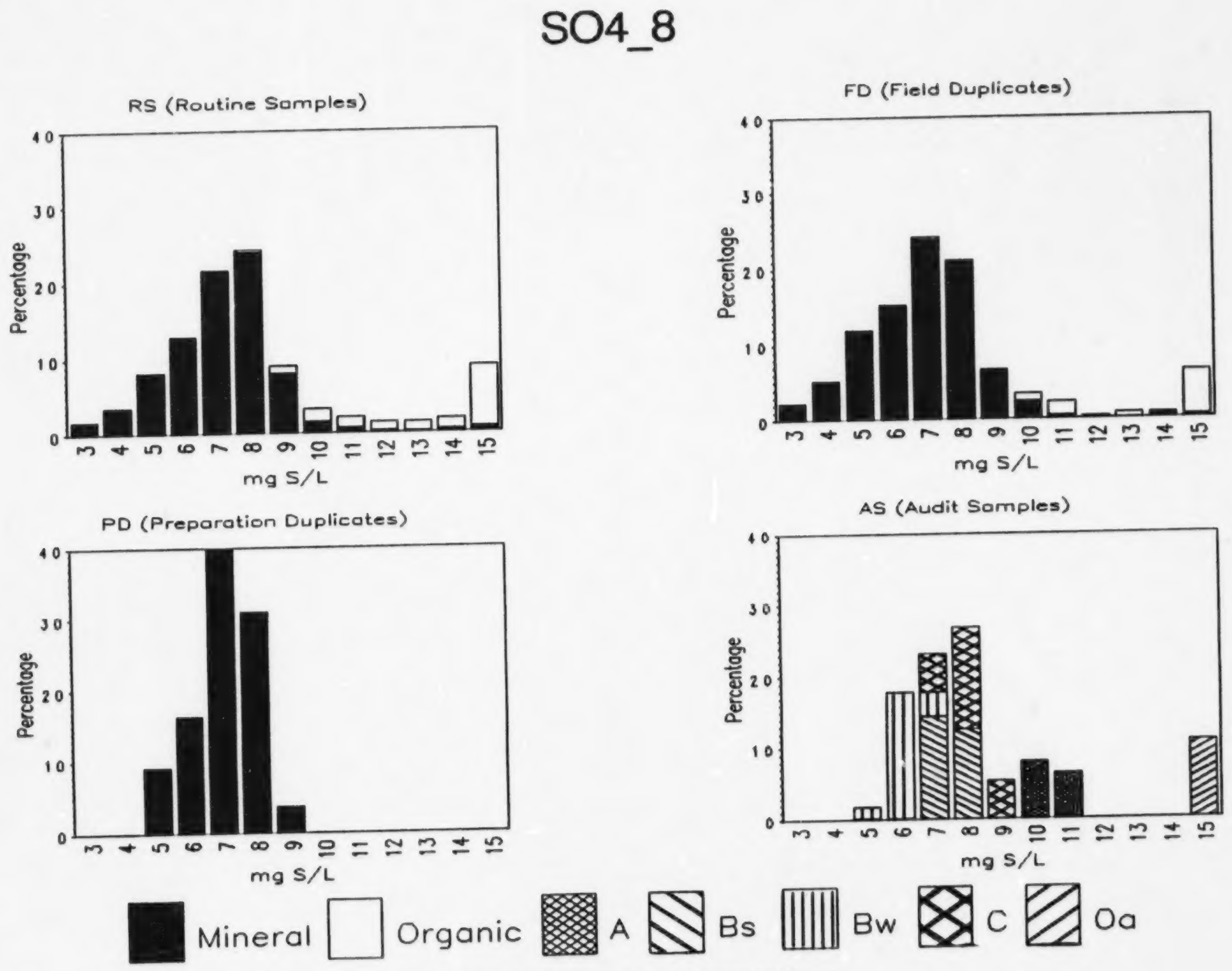


Figure G-46. Range and frequency distribution for the sulfate-eight isotherm.

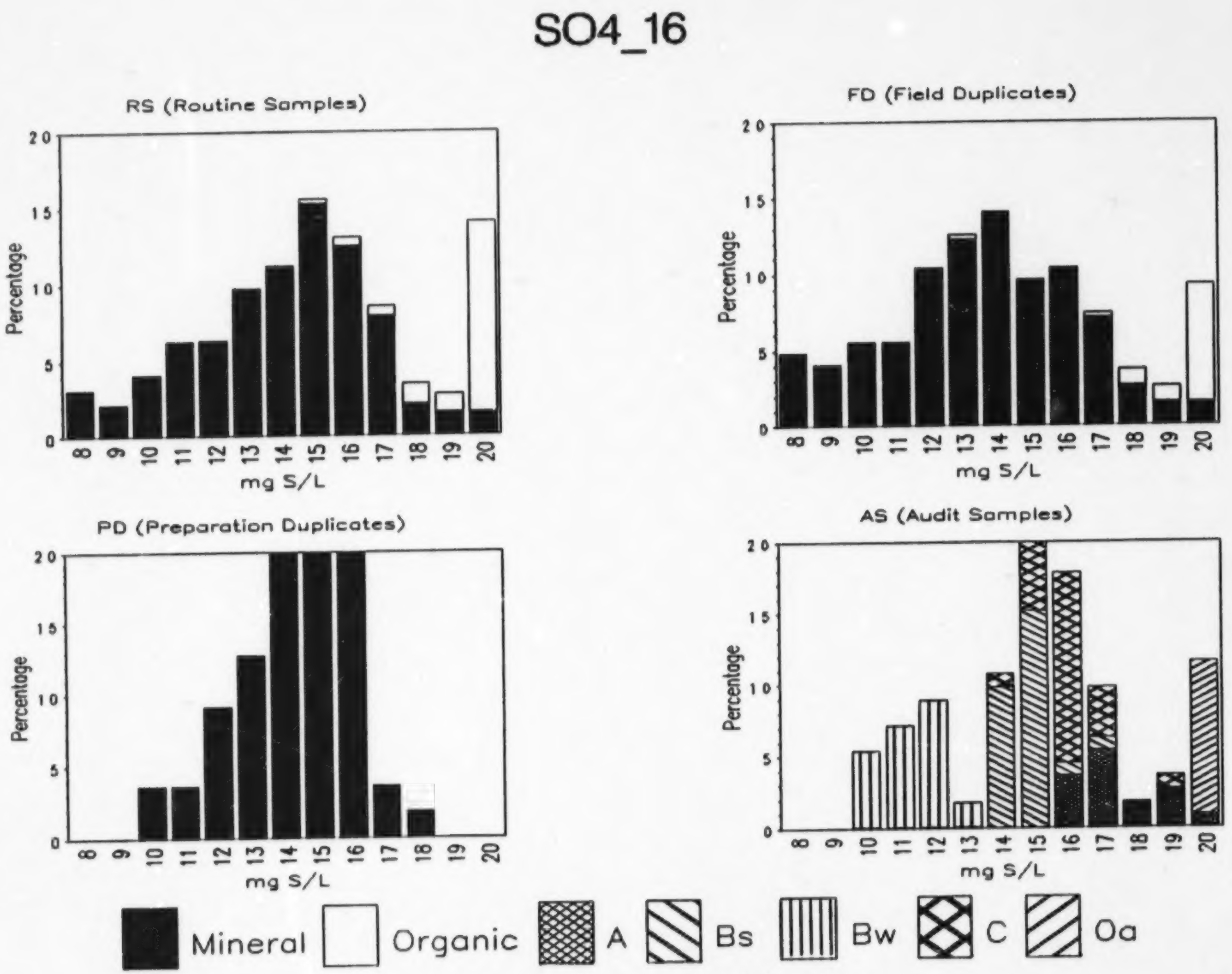


Figure G-47. Range and frequency distribution for the sulfate-16 isotherm.

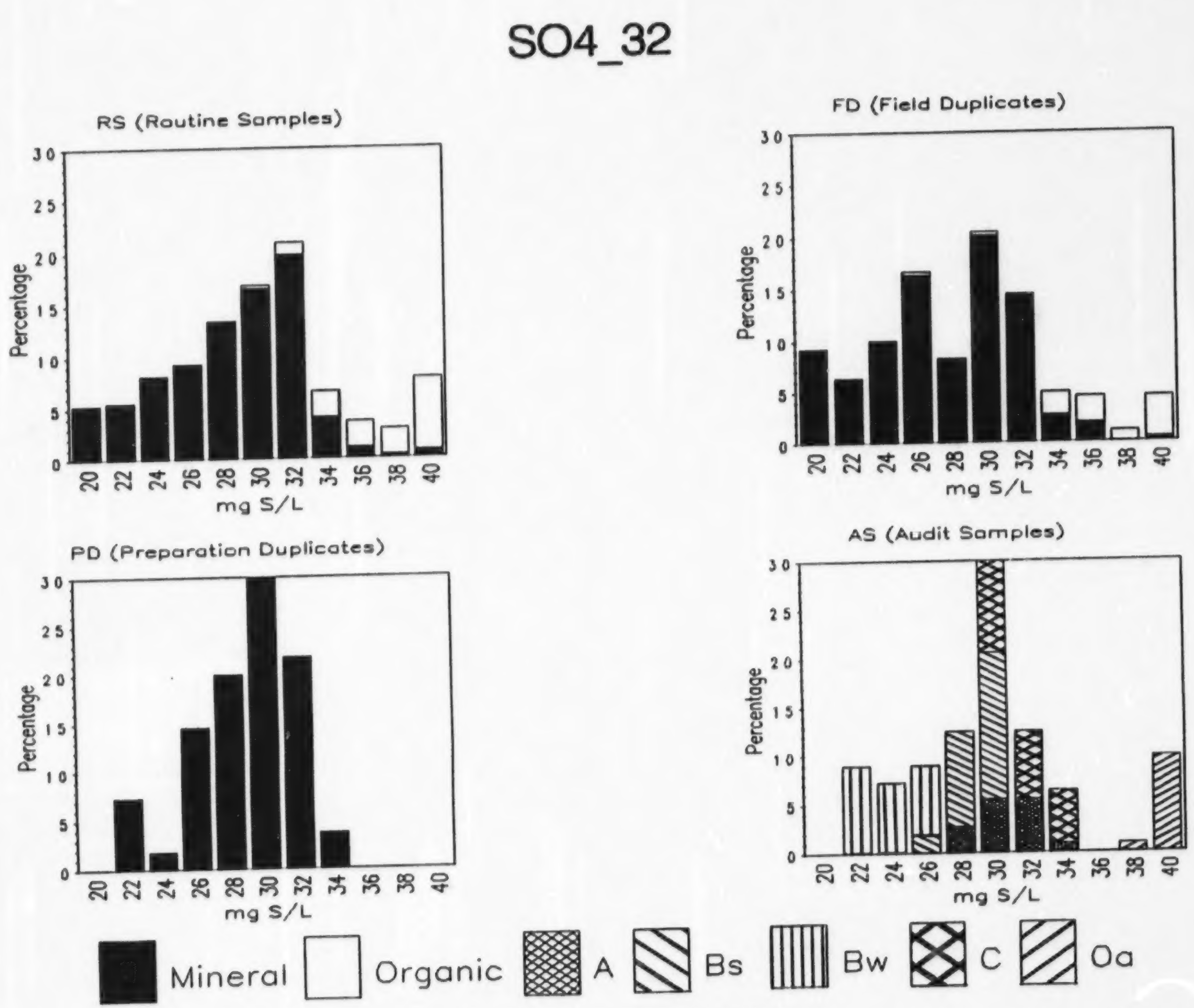


Figure G-48. Range and frequency distribution for the sulfate-32 isotherm.

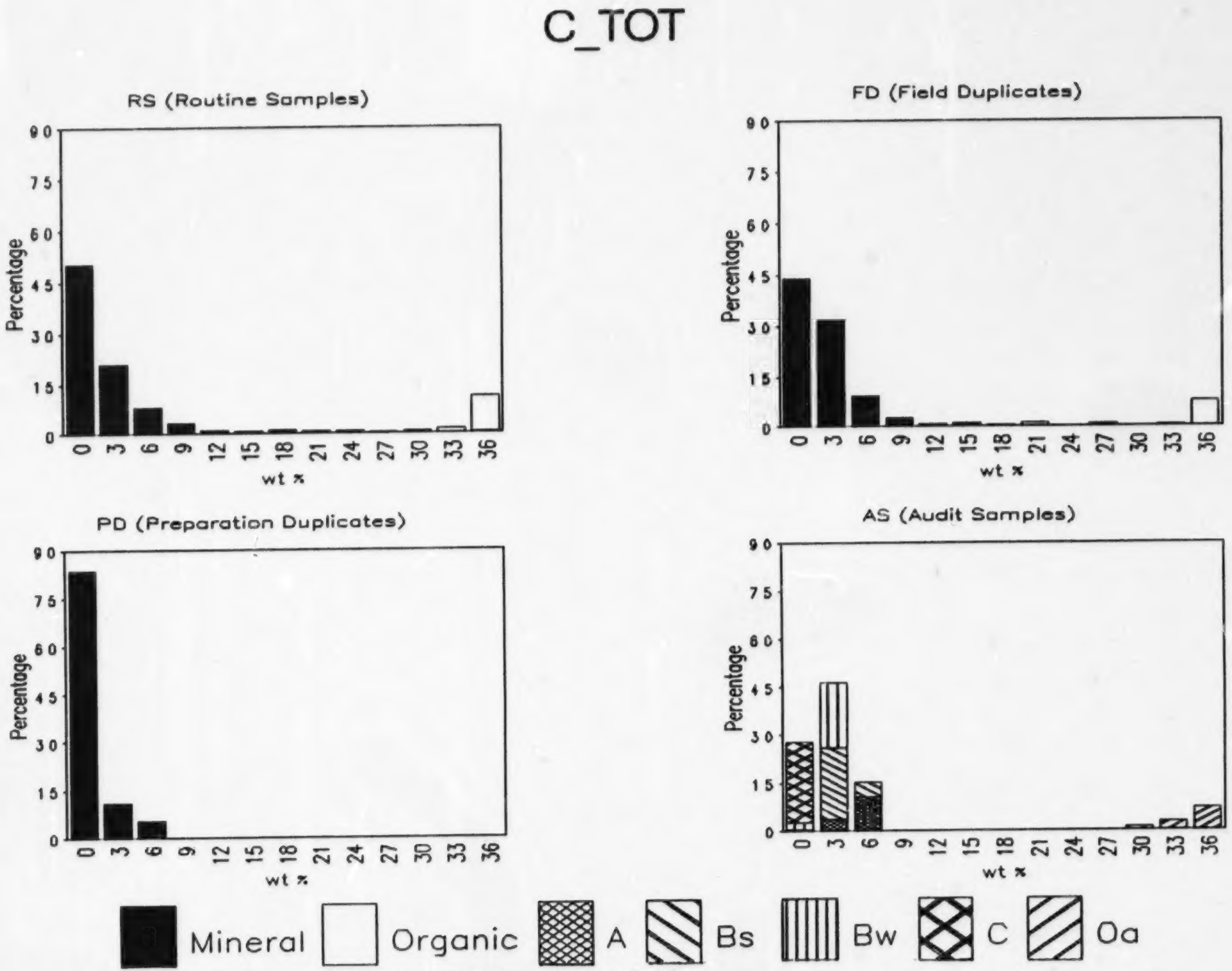


Figure G-49. Range and frequency distribution for total carbon.

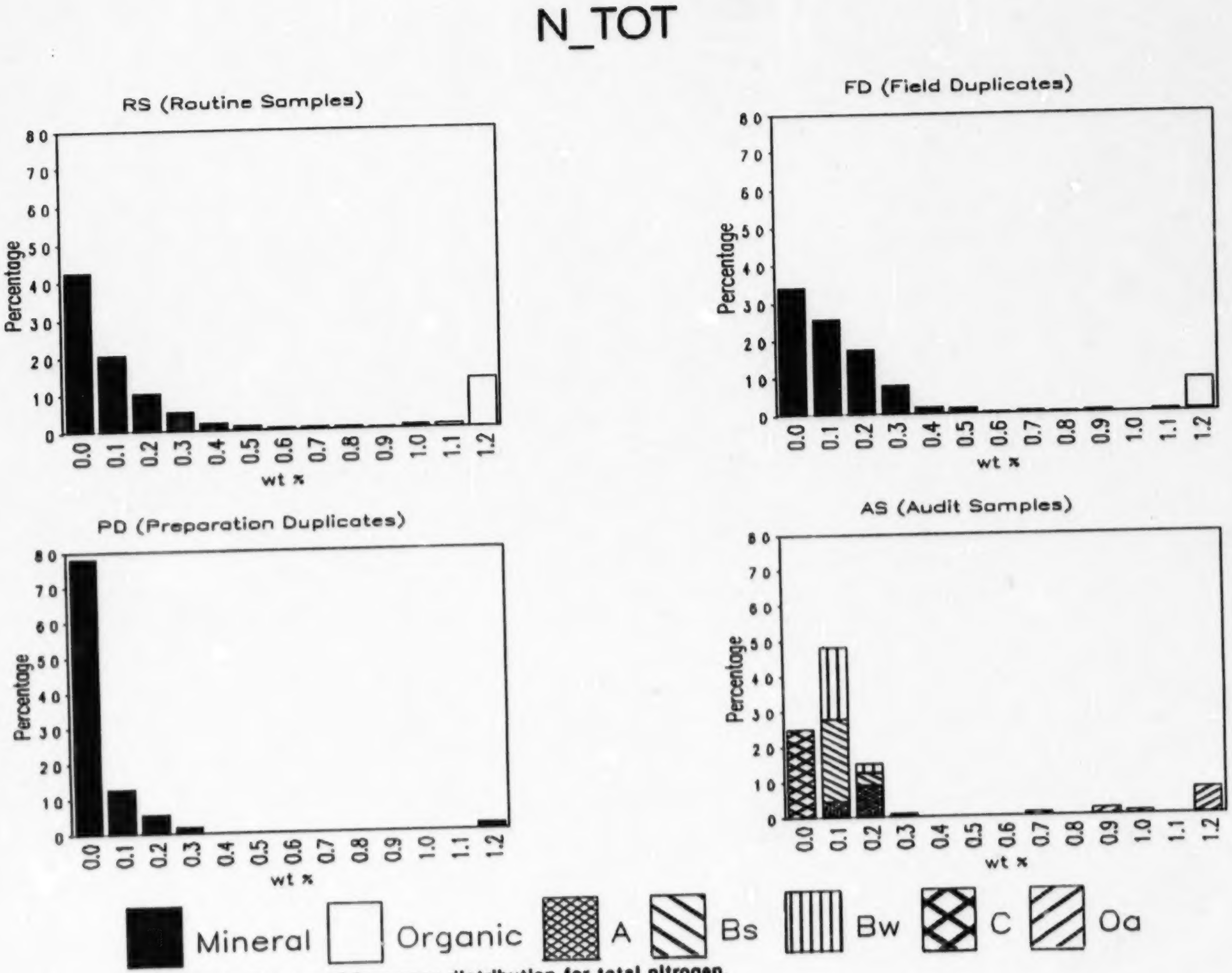


Figure G-50. Range and frequency distribution for total nitrogen.

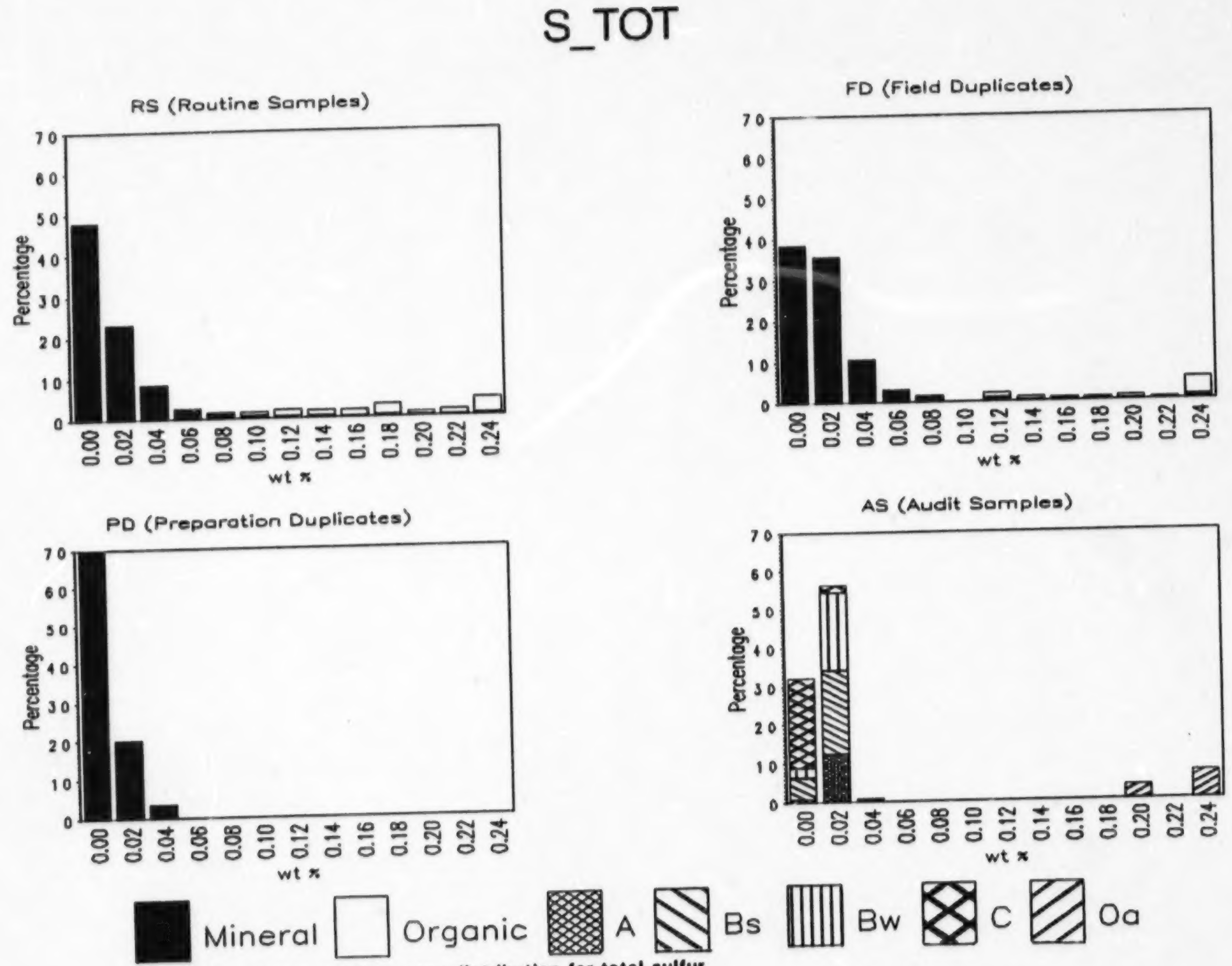


Figure G-51. Range and frequency distribution for total sulfur.